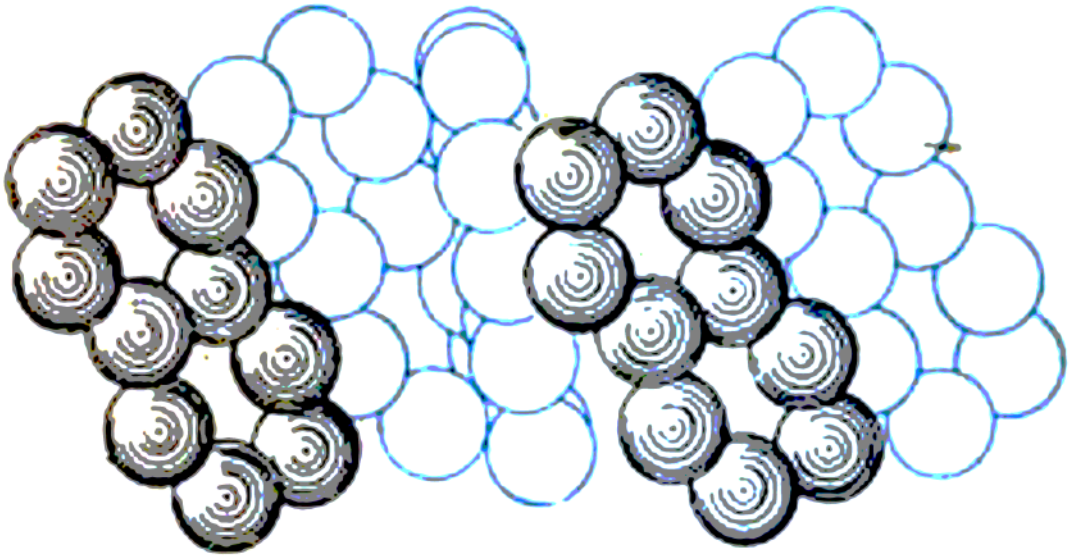
PHYSICAL CHEMISTRY OF POLYMERS

A.Tager



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«ХИМИЯ»
МОСКВА

A. TAGER

PHYSICAL CHEMISTRY OF POLYMERS

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BY
DAVID SOBOLEV AND NICHOLAS BOBROV

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Preface to the Second English Edition

It is very difficult to write a textbook on physical chemistry of polymers, because science is rapidly progressing and many principles are becoming outdated and being replaced by new ones, which are often still not completely proven. From an enormous amount of factual material and theoretical generalizations, it is necessary to take the most fundamental ones, which must be known by those who are becoming acquainted with this field for the first time; this knowledge will help them later to independently cope with the rapid flow of literary information.

The author tried to construct the book on such fundamental material. She may not have always succeeded in this, because the sections of the physical chemistry of polymers are very diverse.

The teaching experience gained in the Soviet institutions of higher education shows that, on the whole, the sections are arranged in correct sequence, and therefore the structure of the book is practically unchanged.

All the chapters have been revised with due account of the new material and some of the well-known principles which were not included in the first edition.

Chapter 5, dealing with polymer structure, has been written anew by G. P. Andrianova. Chapter 16 has been supplemented with a section on the determination of the dimensions and flexibility of macromolecules, being written in collaboration with V. M. Andreyeva.

The book has two new independent chapters on the structure of polymer solutions and the polymerization of mixtures.

CHAPTER 1

Chemical Structure of Monomers and Polymers

1.1. BASIC CONCEPTS AND POLYMER NOMENCLATURE

Polymers are compounds formed by a more or less regular repetition of a large number of the same and different atomic groupings that are joined by chemical bonds into long chains or chains having side branches, and into spatial network as well. According to composition polymers may be classed as organic, inorganic or elemento-organic *. The most thoroughly studied are organic polymers, which are therefore the best material for examining the basic regularities of polymer structure.

The simplest organic polymer is polyethylene, the polymerization product of ethylene. Ethylene is an unsaturated hydrocarbon which enters readily into addition reactions. Two ethylene molecules combine to form a molecule of butene:

$$n\,(CH_2{=}CH_2) \longrightarrow CH_3{-}CH_2{-}(-CH_2{-}CH_2-)_{n-2}{-}CH{=}CH_2$$

The initial substance, ethylene, is called a *monomer*, and the resulting butene is a *dimer*. If three molecules of ethylene combine, the result is a *trimer*, four molecules form a *tetramer*, etc. If n molecules of a monomer unite, they form a *polymer* (from the Greek *poly* meaning many):

$$n CH_2{=}CH_2 \longrightarrow [-CH_2{-}CH_2-]_n$$

The repeating atomic groupings, each of which is a monomeric residue, are called *monomeric units*; a large molecule composed of repeating units ** is called a *macromolecule*, or *polymeric chain.*

* Elemento-organic polymers are also known as hetero-organic polymers. — *Tr.*

** The *repeating unit* of the polymer is usually equivalent or nearly equivalent to the *monomer*, or starting material from which the polymer is formed. For example, the repeating unit of poly(vinyl chloride) is $-CH_2CHCl-$; its monomer is vinyl chloride, $CH_2{=}CHCl$. — *Tr.*

The number of repeating units in the chain is called the *degree of polymerization*, denoted by the letter n or P. The product of the degree of polymerization n and the molecular mass of a monomeric unit M_u equals the molecular mass of the polymer:

$$M_{pol} = nM_u$$

The degree of polymerization may vary over a wide range, from a few units to 5000-10 000 and more. Polymers with a high degree of polymerization are called *high polymers*, while those with a low degree of polymerization are known as *oligomers*. High polymers have very large molecular masses, of the order of from 10^4 to 10^6, and hence, are high-molecular compounds. Oligomers are polymers with a molecular mass of 500-6000.

If the molecular mass of a polymer is high, the terminal or end groups of its chain need not be taken into account, and the polymer molecules can be written without them, showing only a few or even only one monomeric unit. For example, the formula of the polymerization product of ethylene may be represented as follows:

$$\cdots\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}\cdots \quad \text{or} \quad [\text{—}CH_2\text{—}CH_2\text{—}]_n$$

The name of a polymer is usually derived from the name of the monomer by adding to it the prefix *poly*. For instance, the polymerization product of ethylene is known as polyethylene *, that of styrene is called polystyrene, of methyl methacrylate — poly(methyl methacrylate), etc.

A macromolecule may consist of monomers of identical or of different chemical structure. Polymers consisting of identical monomers are called *homopolymers*. Polymeric compounds containing several types of monomeric units in their chain are known as *copolymers*, or *mixed polymers*. Monomeric residues may combine with each other into a macromolecule to form polymers of linear, branched, or crosslinked (three-dimensional) structure.

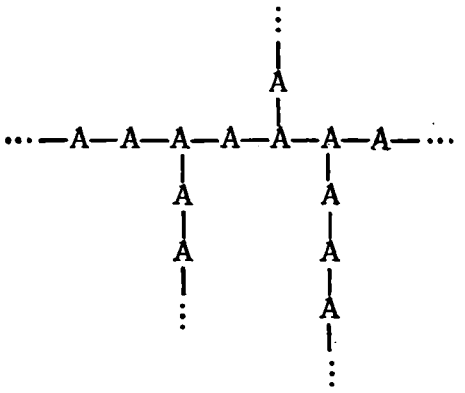
Linear polymers are polymers whose macromolecules are long chains with a high degree of asymmetry. Denoting a monomeric residue by A, one would write the formula of a linear polymer as follows:

$$\cdots\text{—A—A—A—A—A—A—}\cdots$$

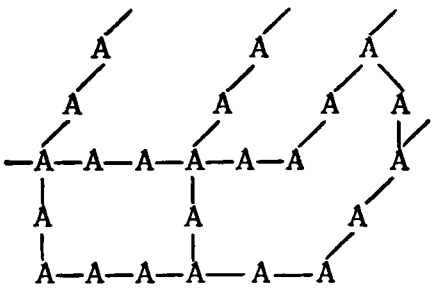
A *branched polymer* is a long chain (usually called the *main*, or *backbone, chain*) with side branches (*side chains*), the number and

* Polyethylene is sometimes called polymethylene, because the repeating unit is the methylene group —CH_2—.

length of which may vary widely:



Crosslinked, or *three-dimensional, polymers* consist of long chains connected up into a three-dimensional network by chemical crosslinks:



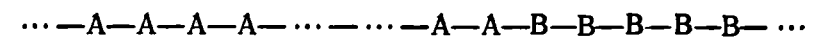
Copolymers may also be linear, branched or crosslinked.

Sometimes three-dimensional polymers are incorrectly called "three-dimensional molecules". A *molecule* is generally understood as the smallest particle of a substance possessing its basic chemical properties and capable of independent existence. A molecule consists of identical or of different atoms, combined into an integral whole by chemical bonds, and always has a definite size. In the case of linear and branched polymers, the molecule concept remains, but is applied to a particle of very large size which can nevertheless be measured. In a three-dimensional polymer all the "molecules" are chemically bound to one another and are incapable of independent existence. If we used the term "three-dimensional molecule", we would logically have to apply the term "molecule" to any piece of three-dimensional polymer, independent of its size, which would be incorrect. Hence, in the case of spatial networks the concept "molecule" loses its physical sense. A network is an unordered chemical combination of a large number of atoms in space.

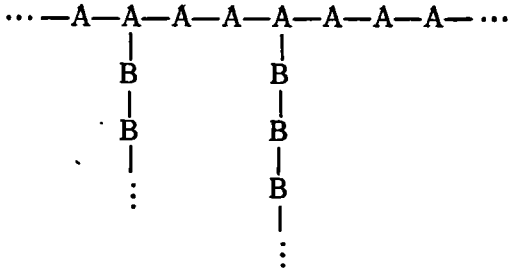
In copolymer molecules the monomer residues may be arranged in the chain at random, according to the laws of chance, or

regularly. Copolymers of the former group are called *statistical* (*irregular*) and those of the latter — *regular.*

Linear copolymers in which the units of each type form fairly long continuous sequences (*blocks*) are known as *block copolymers*:

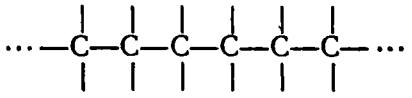


Branched copolymers with monomers of one kind in their main chain and monomers of another in their side branches are called *graft copolymers*:

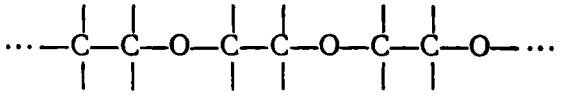


According to the structure of their main chain all polymers fall into homochain and heterochain polymers.

The main chains of *homochain polymers* are composed of atoms of the same species, e. g., carbon, sulphur, phosphorus, etc. If the main chain of the macromolecule consists only of carbon atoms, the compound is called a *carbon-chain polymer*:



In *heterochain polymers* the main chain is made up of different atoms, e.g.



1.2. CLASSIFICATION OF POLYMERS

The ability of an element to form polymeric compounds depends on its position in the Mendeleev Periodic System.

The elements of group one and the univalent elements of other groups (hydrogen, the halogens) are entirely incapable of forming polymers, because to form a chain an element must have at least two valencies. All the other elements can give homochain or heterochain polymeric compounds, the stability of which depends on the interatomic bond strength.

Tables 1.1 and 1.2 give the bond energies between some like and unlike atoms.

TABLE 1.1 *Bond Energy Between Like Atoms (Homochain Polymers)*

Bond	Bond energy, kcal/mole	Bond	Bond energy, kcal/mole	Bond	Bond energy, kcal/mole
C—C	80.0	Se—Se	50.0	Ge—Ge	39.2
S—S	63.0	Te—Te	49.0	As—As	39.0
P—P	53.0	Si—Si	45.0	N—N	37.0
		Sb—Sb	42.0	O—O	34.0

TABLE 1.2. *Bond Energy Between Unlike Atoms (Heterochain Polymers)*

Bond	Bond enegy, kcal/mole	Bond	Bond energy, kcal/mole	Bond	Bond energy, kcal/mole
B—O	119.3	P—O	81.7	Al—C	61.6
B—N	104.3	C—O	79.0	C—S	61.5
Si—O	89.3	C—N	66.0	Si—S	60.9
B—C	89.0	As—O	64.5	C—Si	57.6

It is evident from Table 1.1 that the strongest bonds are those between carbon atoms and the weakest, between nitrogen and oxygen atoms. This evidently accounts for the fact that homochain polymeric compounds of oxygen and nitrogen cannot be produced. All the other elements can form homochain polymers.

A much larger number of elements can participate in the formation of heterochain polymeric compounds. Bond energies between the atoms in heterochain compounds are higher than in many homochain compounds (see Table 1.2). Especially strong bonds are those formed between boron and oxygen or nitrogen, and between silicon and oxygen. Polymeric compounds with such bonds are very strong high-melting substances.

It has been stated above that polymers may be classed as organic, elemento-organic (or hetero-organic), and inorganic. However, it is very difficult to draw sharp boundary between these three classes, because there are many different compounds intermediate between them. The classification of polymers adopted in this book is based on their chemical composition. It was suggested by Berlin and Parini.

Organic polymers include compounds containing, apart from carbon atoms, hydrogen, oxygen, nitrogen, sulphur, and halogen atoms, even if the oxygen, nitrogen, or sulphur is in the backbone chain.

Organic polymers also include polymeric substances containing other elements in their molecules provided the atoms of these elements are not in the main chain and are not connected directly to carbon atoms (e.g., organic polyacid salts).

Elemento-organic, or *hetero-organic, polymers* include:

(a) compounds whose chains are composed of carbon atoms and hetero-atoms (except for nitrogen, sulphur, and oxygen atoms);

(b) compounds with inorganic chains if they contain side groups with carbon atoms connected directly to the chain;

(c) compounds whose main chains consist of carbon atoms and whose side groups contain hetero-atoms (except for nitrogen, sulphur, oxygen, and halogen atoms) connected directly to the carbon atoms of the chain.

Inorganic polymers are polymers containing no carbon atoms.

The question as to which inorganic compounds should be classed as polymers is not quite clear as yet. In solving this question one of the main factors that have to be taken into account is evidently the type of bond characteristic of the compound under consideration. For example, metals are not classed as polymers, because they are characterized by what is known as the metallic bond, meaning combination of ions in the crystal through free mobile electrons. Ordinary salts are not polymers either, because though they possess ionic chemical bonds, salts dissociate into ions in dilute solutions.

Compounds that should be classed as inorganic polymers are those whose chains are composed of different atoms joined by chemical bonds, while weaker intermolecular forces act between the chains.

As has already been said, the elements of group I do not form polymeric compounds; those of group II (beryllium, cadmium, etc.) form heterochain polymers. For instance, magnesium oxide has the following polymeric structure:

$$\cdots\text{—Mg—O—Mg—O—Mg—O—}\cdots$$

Especially important are the heterochain polymeric compounds of group III and group IV elements.

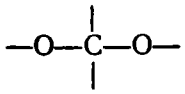
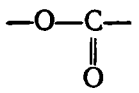
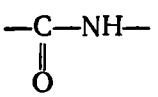
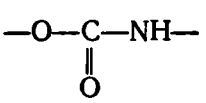
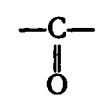
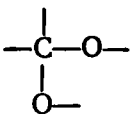
Given below are the most important organic, elemento-organic and inorganic polymers whose physicochemical properties are discussed later on in this book.

1.2.1. Organic and Elemento-Organic Polymers

In accordance with the classification accepted in organic chemistry, organic polymers fall into *aliphatic* and *aromatic* ones. Depending on the nature of a substituent, each of these classes

may be divided into hydrocarbons, halogen derivatives, alcohols, acids, ethers and esters, nitriles, aldehydes, ketones, and so forth. These classes are characteristic of homochain polymers. Heterochain polymers are divided into classes according to the chemical nature of a grouping that is repeated in the chain itself. Table 1.3

TABLE 1.3. *Classes of Heterochain Polymers*

Grouping	Formula	Polymer class
Ether		Polyethers
Ester		Polyesters
Amide		Polyamides
Urethane		Polyurethanes
Anhydride		Polyanhydrides
Acetal		Polyacetals

gives the most typical groupings that are repeated in a chain and the names of the appropriate polymeric classes.

The chemical formulas of some heterochain and homochain polymers are given in Table 1.4. The radicals R which stand between the repeating groupings may be aliphatic and aromatic, i.e., aromatic groups are not only substituents, as is the case in the molecules of polystyrene or poly-α-methylstyrene; they may also be in the skeleton of the chain itself. The latter may be composed of only aromatic noncondensed and condensed nuclei.

Aromatic polymers are now widely used, since in most cases they are heat-resistant, and this is very important to modern technology. In particular, high-strength thermostable fibres are produced from them.

TABLE 1.4. *Organic Polymers*

Polymer	Repeating unit	Monomer	Chemical formula of monomer
	Homochain Polymers		
Polymeric Saturated Hydrocarbons			
Polyethylene	$-CH_2-CH_2-$	Ethylene	$CH_2=CH_2$
Polypropylene	$-CH_2-CH(CH_3)-$	Propylene	$CH_2=CH(CH_3)$
Polybutylene	$-CH_2-CH(C_2H_5)-$	Butylene	$CH_2=CH(C_2H_5)$
Polyisobutylene	$-CH_2-C(CH_3)_2-$	Isobutylene	$CH_2=C(CH_3)_2$
Polymeric Unsaturated Hydrocarbons			
Polybutadiene	$-CH_2-CH=CH-CH_2-$	Butadiene	$CH_2=CH-CH=CH_2$
Polyisoprene	$-CH_2-C(CH_3)=CH-CH_2-$	Isoprene	$CH_2=C(CH_3)-CH=CH_2$
Halogenated Polymers			
Poly(vinyl chloride)	$-CH_2-CHCl-$	Vinyl chloride	$CH_2=CHCl$
Poly(vinylidene chloride)	$-CH_2-CCl_2-$	Vinylidene chloride	$CH_2=CCl_2$
Polytetrafluoroethylene	$-CF_2-CF_2-$	Tetrafluoroethylene	$CF_2=CF_2$

Polytrifluorochloroethylene	$-CF_2-CFCl-$	Trifluorochloroethylene	$CF_2=CFCl$
Polychloroprene	$-CH_2-\underset{\displaystyle Cl}{\underset{\vert}{C}}=CH-CH_2-$	Chloroprene	$CH_2=\underset{\displaystyle Cl}{\underset{\vert}{C}}-CH=CH_2$

Polymeric Alcohols and Their Derivatives

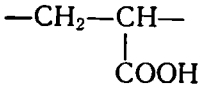
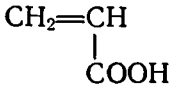
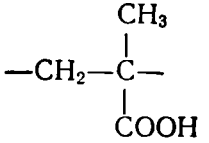
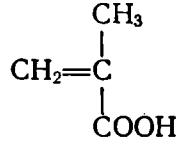
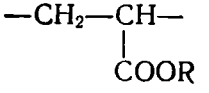
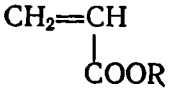
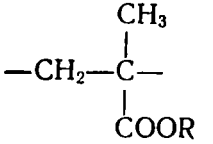
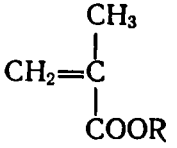
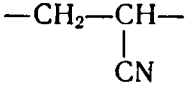
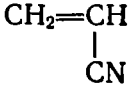
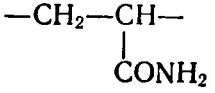
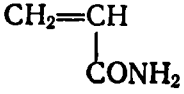
Poly(vinyl alcohol)	$-CH_2-\underset{\displaystyle OH}{\underset{\vert}{CH}}-$	—	—
			$CH_2=\underset{\displaystyle CH_2OH}{\underset{\vert}{CH}}$
Poly(allyl alcohol)	$-CH_2-\underset{\displaystyle CH_2OH}{\underset{\vert}{CH}}-$	Allyl alcohol	
Poly(vinyl ethers)	$-CH_2-\underset{\displaystyle OR}{\underset{\vert}{CH}}-$	Vinyl ethers	$CH_2=\underset{\displaystyle OR}{\underset{\vert}{CH}}$
Poly(vinyl esters) *	$-CH_2-\underset{\displaystyle OCOR}{\underset{\vert}{CH}}-$	Vinyl esters	$CH_2=\underset{\displaystyle OCOR}{\underset{\vert}{CH}}$

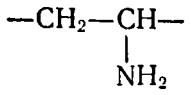
Polymeric Aldehydes and Ketones

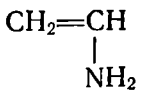
Polyacrolein	$-CH_2-\underset{\displaystyle CHO}{\underset{\vert}{CH}}-$	Acrolein	$CH_2=\underset{\displaystyle CHO}{\underset{\vert}{CH}}$
Polymethylvinyl ketone	$-CH_2-\underset{\displaystyle COCH_3}{\underset{\vert}{CH}}-$	Vinyl ketone	$CH_2=\underset{\displaystyle COCH_3}{\underset{\vert}{CH}}$

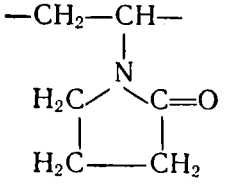
* The names of poly(vinyl esters) are derived from the name of the acid radical, e. g., poly(vinyl formate), poly(vinyl acetate), poly(vinyl butyate), etc.

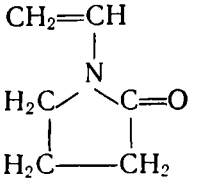
Table 1.4 (*cont'd*)

Polymer	Repeating unit	Monomer	Chemical formula of monomer
Polymeric Acids and Their Derivatives			
Poly(acrylic acid)		Acrylic acid	
Poly(methacrylic acid)		Methacrylic acid	
Polymers of acrylic acid esters (polyacrylates) *		Acrylates	
Polymers of methacrylic acid esters (polymethacrylates) *		Methacrylates	
Polyacrylonitrile		Acrylonitrile	
Polyacrylamide		Acrylamide	

Poly(vinyl amine) 

Vinyl amine 

Poly(vinyl pyrrolidone) 

N-Vinyl pyrrolidone 

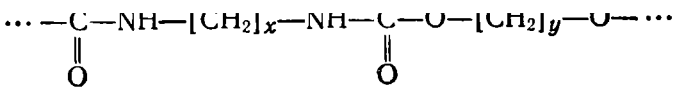
Polymer	Polymer chain structure
Heterochain Polymers	
Polymers Containing Oxygen in Their Main Chain	
Polyethers	$\cdots\text{--}[CH_2]_n\text{—O—}[CH_2]_m\text{—O—}\cdots$
Polyformaldehyde	$\cdots\text{—}CH_2O\text{—}\cdots$
Poly(propylene oxide)	$\cdots\text{—}CH_2\text{—}CH(CH_3)\text{—O—}\cdots$

* Polyacrylates and polymethacrylates are named according to the radical they contain: poly(methyl acrylate), poly(ethyl acrylate), poly(methyl methacrylate), poly(ethyl methacrylate), poly(butyl methacrylate), etc.

Table 1.4 (*cont'd*)

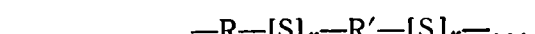
Polymer	Polymer chain structure
Polyesters	$\cdots -[CH_2]_m-\underset{\underset{O}{\|}}{C}-O-[CH_2]_n-O-\underset{\underset{O}{\|}}{C}-\cdots$
Polycarbonates	$\cdots -O-R-O\underset{\underset{O}{\|}}{C}-\cdots$
Polyanhydrides	$\cdots -\underset{\underset{O}{\|}}{C}-R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R-\underset{\underset{O}{\|}}{C}-\cdots$ (R = aliphatic or aromatic radical)
Epoxy polymers	$\cdots -O-R-O-CH_2-\overset{\overset{OH}{\|}}{CH}-CH_2-\cdots$
Polymers Containing Nitrogen in Their Main Chain	
Polyamides	$\cdots -NH-[CH_2]_x-NH-\underset{\underset{O}{\|}}{C}-[CH_2]_y-\underset{\underset{O}{\|}}{C}-\cdots$
	$\cdots -NH-Ar-NH-\underset{\underset{O}{\|}}{C}-Ar-\underset{\underset{O}{\|}}{C}-\cdots$

Polyurethanes



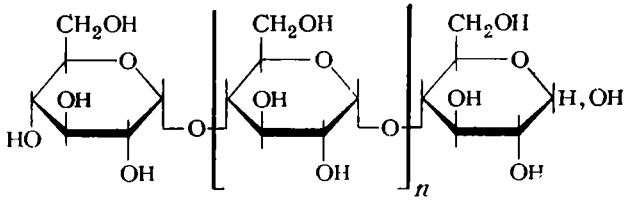
Polymers Containing Sulphur in Their Main Chain

Polysulphides



Polyacetals

Starch



Cellulose

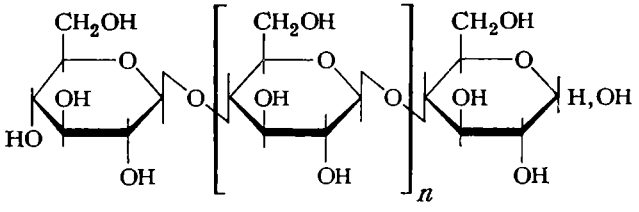
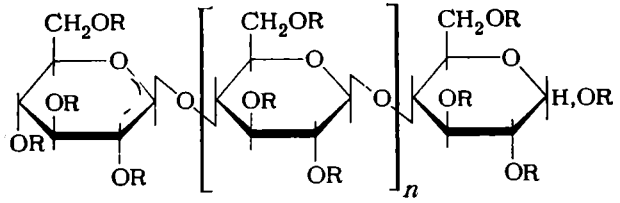
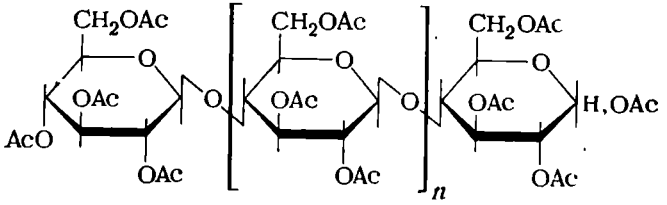
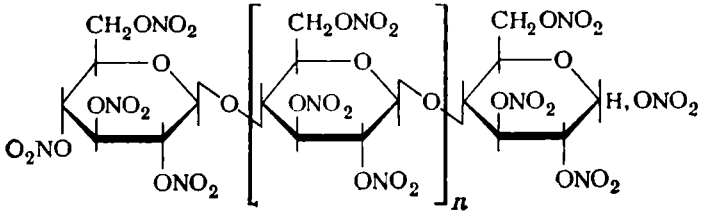
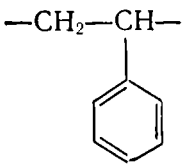


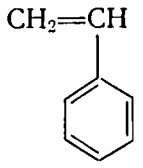
Table 1.4 (*cont'd*)

Polymer	Polymer chain structure
Cellulose ethers	 (R = methyl-, ethyl-, propyl-, benzyl-, etc.)
Cellulose esters	 where Ac = $-COCH_3$
Cellulose nitrate	

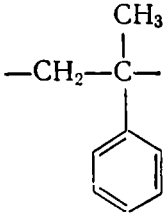
Polystyrene



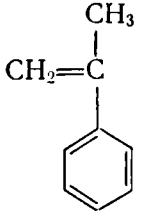
Styrene



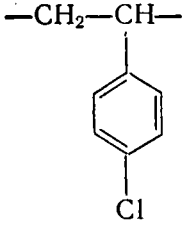
Poly-α-methylstyrene



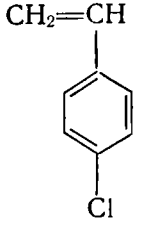
α-Methylstyrene



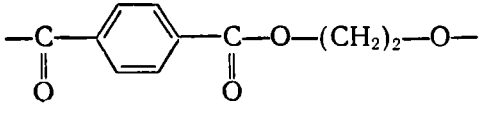
Polyparachlorostyrene



Chlorostyrene



Polyethylene terephthalate



Terephthalic acid

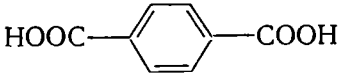
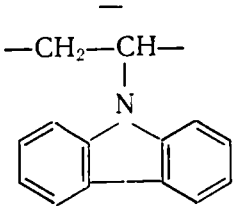
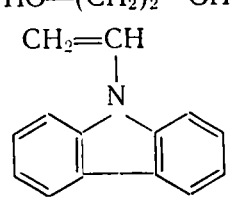
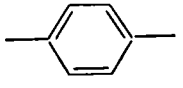
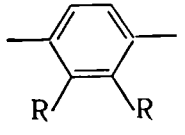
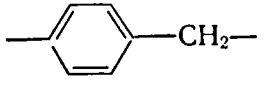
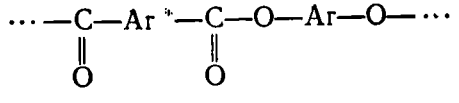
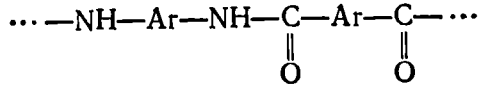
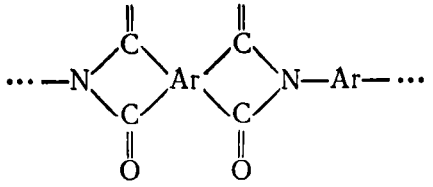


Table 1.4 (*cont'd*)

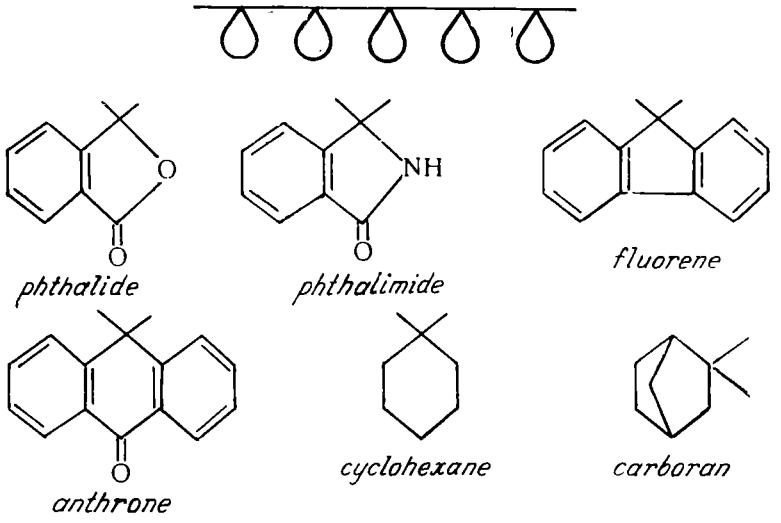
Polymer	Repeating unit	Monomer	Chemical formula of monomer
—	—	Ethylene glycol	$HO-(CH_2)_2-OH$
Poly(vinyl carbazole)		N-Vinyl carbazole	

Polymer	Repeating unit
Polyphenylenes	
Substituted polyphenylenes	
Polymethylenephenylenes	
Polyarylates	
Polyamides	

Polyimides **



V. V. Korshak, S. V. Vinogradova and their co-workers are developing the synthesis of aromatic "*cardo*" *polymers*, which combine high thermal stability with good solubility. The name of the polymers is derived from the Latin word *cardo*, which means "loop", since the groupings in the repeating units may be regarded as loops in respect of the main chain:

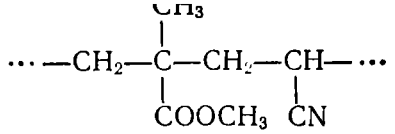


* The radical Ar (aryl) may be a residue of any aromatic dicarboxylic acids, bisphenols or diamines.
** Polyimides may be synthesized from any tetracarboxylic acids.

Table 1.4 (*cont'd*)

Polymer	Polymer chain structure
	Conjugated-Bond Polymers
Polyacetylenes (polyvinylenes)	$\cdots$—CH=CR—CH=CR—CH=CR—$\cdots$ (R = C_6H_5, $COCH_3$ or H)
Polyphenylenes	See above
	Polymers Built Only from Carbon Atoms
α-carbin	—C≡C—C≡C—
β-carbin	=C=C=C=C=C=
	Copolymers
Butadiene-styrene copolymers	$\cdots$—CH_2—CH=CH—CH_2—CH_2—CH(C_6H_5)—$\cdots$
Butadiene-acrylonitrile copolymers	$\cdots$—CH_2—CH=CH—CH_2—CH_2—CH(CN)—$\cdots$
Bytadiene-isobutylene copolymers	$\cdots$—CH_2—CH=CH—CH_2—CH_2—C(CH_3)(CH_3)—$\cdots$
Vinyl chloride-vinylidene chloride copolymers	$\cdots$—CH_2—CHCl—CH_2—CCl_2—$\cdots$
Vinyl chloride-vinyl acetate copolymers	$\cdots$—CH_2—CHCl—CH_2—CH($OCOCH_3$)—$\cdots$

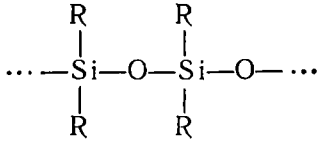
Methyl methacrylate-acrylonitrile copolymers



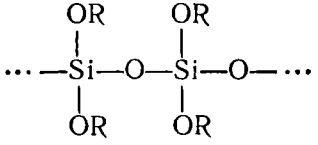
Elemento-Organic Compounds

Siliconorganic Polymers

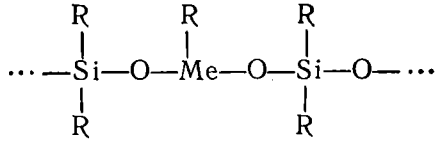
Polysiloxanes



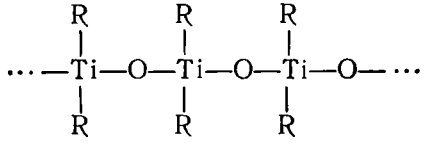
Polymeric esters of orthosilicic acid



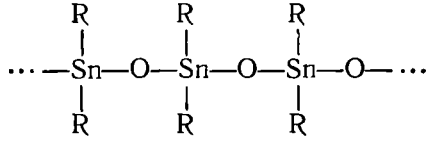
Poly(elemento-organic siloxanes)



Polytitanoxanes

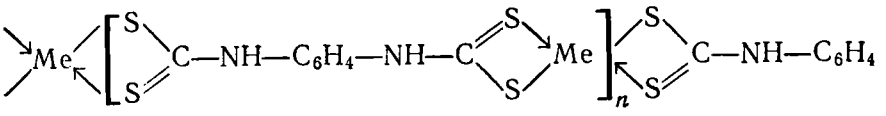


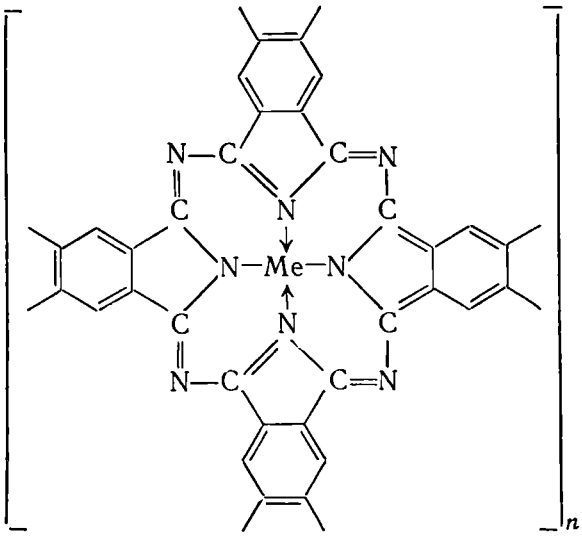
Polystananoxanes



1.2.2. Coordination, or Chelate, Polymers

Coordination (chelate) polymers are high-molecular substances whose main chain is built from units which represent chelate rings. A chelate ring is formed from an ion of metal (chelating agent) and different organic ligands which have a donor-acceptor bond between them. The formulas of some chelate polymers in which Zn, Ni, Cd, Cu, and Fe may be chelating agents are given below:



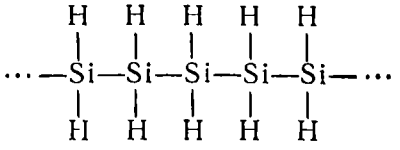


These polymers withstand heating up to 350 °C and possess semiconductor properties.

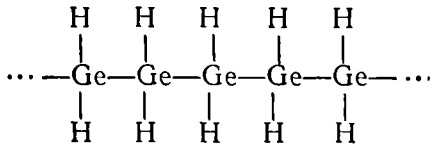
1.2.3. Inorganic Polymers

Inorganic polymers have been studied very little so far and it is difficult to divide them into classes at present. For this reason only the most typical inorganic polymers containing elements of the IV-VI groups of the Periodic Table are enumerated below.

Homochain Polymers of IV-VI Group Elements. All the elements of group IV can form linear chains, analogous to those of polyethylene:



Polysilanes



Polygermanes

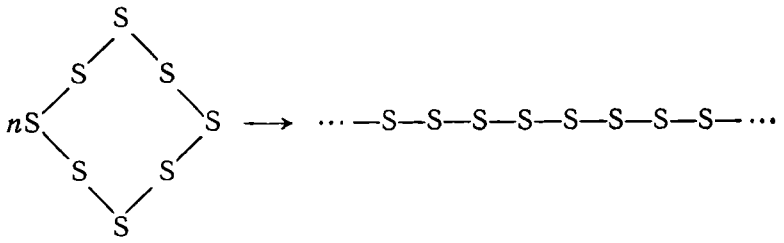
The elements of group V usually form low-molecular compounds, but under certain conditions they can change into polymers.

White phosphorus consists of P_4 molecules arranged in the form of a tetrahedron. When heated it passes into a polymer. *Red phosphorus* results when the white modification is heated to 500 °C. This is a less ordered form of polymeric phosphorus. The most ordered form is *black phosphorus* which forms from white phosphorus when the latter is heated at 200 °C and 12 000 atm. It is a polymeric compound with a lamellar lattice like that of graphite.

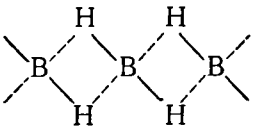
Arsenic forms an amorphous polymer when heated at comparatively low temperatures and a rhombohedric crystalline polymer when heated at 270 °C. Polymeric forms of antimony are known, analogous to those of red phosphorus and arsenic.

Sulphur and *selenium* (group VI) have a high tendency to form linear homochain polymeric compounds.

Ordinary *rhombohedric sulphur* has cyclic molecules containing eight sulphur atoms each. When sulphur is heated in the molten state, the ring opens into a linear polymer:

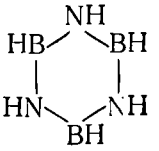


Heterochain Polymers. The compounds discussed below are heterochain polymers of III and IV group elements. For example, *hydrogen boride* has the following polymeric structure:



Boron nitride is a polymer of graphite-like structure.

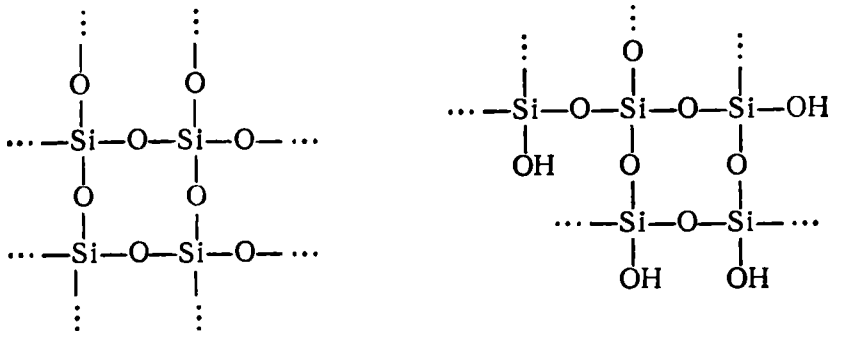
Borazole



polymerizes at room temperature.

Typical polymers are amorphous

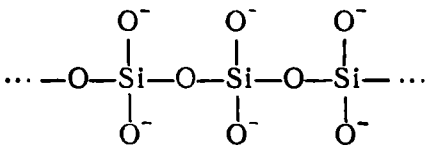
silicon dioxide and *polysilicic acid*



Natural and synthetic silicates and aluminosilicates also possess polymeric structure.

Silicates are salts of silicic acid, having the generic formula $xE_nO_m \cdot ySiO_2 \cdot zH_2O$, E representing Na, Ca, Al, Mg, and other similar atoms.

In most silicates the atoms in the chain are linked by covalent bonds, and the chains are connected by ionic bonds



Such a chain is known as a *pyroxene chain.*

Silicates may be of lamellar or three-dimensional crystalline structure (e.g., quartz). Some lamellar silicates are *talc* $Si_8O_{20}Mg_6(OH)_4$ and some varieties of *natural asbestos*, such as chrysotile asbestos $Mg_6(Si_4O_{11})(OH)_6 \cdot H_2O$.

Of polymeric structure are silicate glasses, whose main constituent is SiO_2. The presence of metals (K and Na) in glass disturbs its crystalline structure and that is why silicate glasses are amorphous under ordinary conditions.

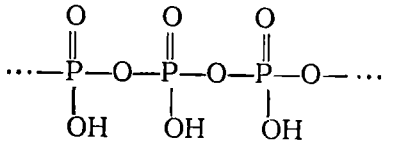
Other noteworthy polymeric compounds of this type are *cement* (the generic name given to numerous mineral binders), which consists mainly of various silicates, and *concrete.*

Some natural aluminosilicates of lamellar structure are *kaolinites*, *montmorillonites*, and *zeolites.* Synthetic zeolites are called *permutites*; an example of the latter is sodium permutite

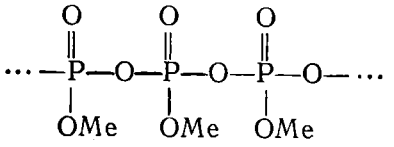
$$Na_2O \cdot CaO \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$$

Of the polymeric inorganic compounds of V and VI group elements the following should be mentioned:

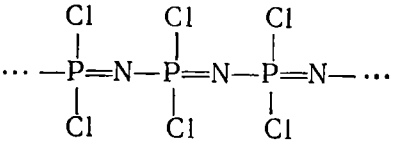
Polyphosphoric acids



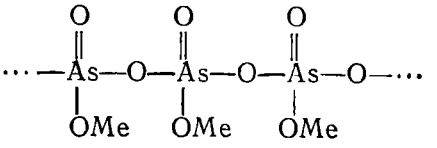
Polyphosphates



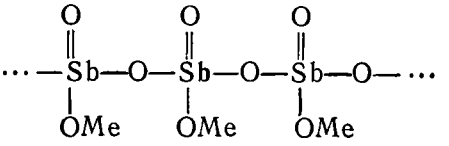
Poly(phosphonitrile chloride)



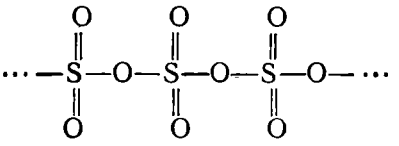
Polyarsenates



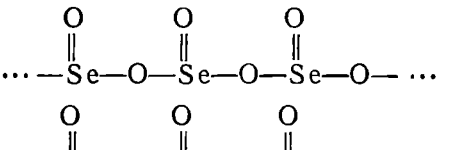
Polystibnates



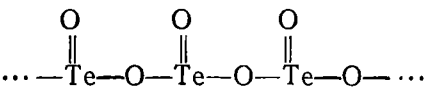
Sulphur-containing polymers



Selenium-containing polymers

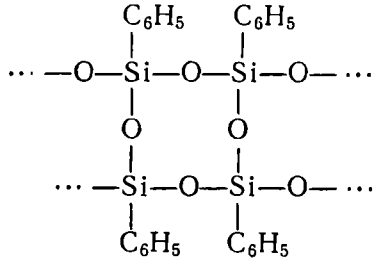


Tellurium-containing polymers



In examining the classification of polymers according to the chemical structure, it is expedient to dwell on some names which are accepted in polymer chemistry and which are often found in literature. For example, polymeric compounds in whose chain the radical vinyl $CH_2=CH-$ is repeated are known as *vinyl polymers*. They include poly(vinyl alcohol) and all its derivatives, polystyrene and its derivatives, and polyalkylacrylates. Polymers whose macromolecules contain side branches (mainly of the hydrocarbon type) in every elementary unit, being joined by different chemical groups (holding regions) with the main polymer chain, are known as *comb-like polymers*. Examples of such polymers are

the higher homologues of poly-α-olefins, poly-*n*-alkylacrylates, and poly-*n*-alkyl ethers and poly-*n*-alkyl esters. Branched polymers whose macromolecules resemble a star by their structure are known as *star-like polymers*. Cyclolinear double-chain polymers are known as *ladder polymers*. An example is ringlinear polyphenylsiloxane, which has the following structure:



The configuration of its double-chain macromolecule is given in Fig. 1.1.

Apart from classification according to the chemical structure, polymers may be divided into *natural* and *synthetic* ones. Natural

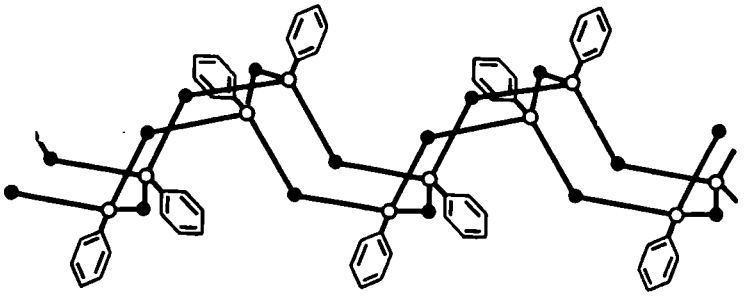
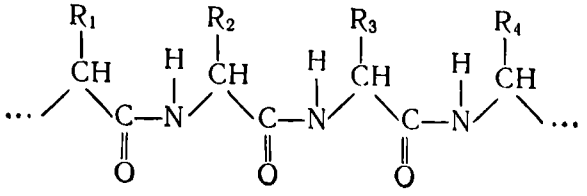


Fig. 1.1. Configuration of ring-linear polyphenylsiloxane molecule

polymers include natural rubber and gutta-percha, whose macromolecules are built from the residues of isoprene (polyisoprenes), cellulose, starch, proteins, and nucleic acids.

Proteins are high-molecular compounds consisting of many hundreds and even thousands of amino acid units. Their molecular mass reaches several millions. Proteins are linear polymers, or copolymers, to be more exact, which consist of the residues of amino acids, differing by the nature of the side radical R_i. They are known as *biopolymers*:



Proteins have, in all, 20 of the most universal, "magic" amino acids and up to ten of the rarer amino acids. These amino acids alternate differently in the macromolecules of different proteins. The chemical structure of many proteins has been deciphered. However, the exact formulas of many proteins used industrially are still unknown. This applies to casein, keratin, collagen, gelatin and agar.

Casein is a complex protein, which forms from caseinogen (the most important component of milk, curds, and cheese) when it curdles under the action of enzymes. Apart from carbon, hydrogen, oxygen, and nitrogen, casein contains phosphorus.

Keratins are the main constituents of integumentary and protective tissues of animal organisms (skin, horn, hair, and wool). Keratins are characterized by a high sulphur content.

Collagen is the main constituent of connective tissue; in particular, a large amount of collagen is contained in the bones of animals.

Gelatin, a mixture of animal proteins, is obtained in industry by subjecting bones, horns, and hides of animals to special treatment. Another product used widely in industry along with gelatin is *agar*, made from certain species of sea weeds. *Agar* is up to 85-90 per cent carbohydrates, mainly polysaccharides (pentosans, hexosans, and galactans).

Hence, the variety of natural polymers is limited. Man turned out to be more inventive than nature, having synthesized a large number of polymers in factories and laboratories. The producer of the first synthetic rubber S. V. Lebedev correctly said that there was no limit to this diversity.

1.3. SPECIFIC FEATURES OF POLYMER STRUCTURE

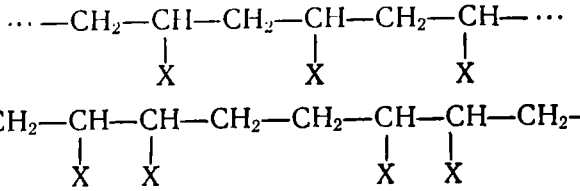
Polymers may be regular or irregular, chemically homogeneous or heterogeneous, and mono- or polymolecular (mono- or polydisperse).

1.3.1. Regular and Irregular Polymers

A polymer with chains that are monotonic alternations of repeating units, i.e., having a perfect long-range order of units, is of *regular structure*. Any polymer that lacks such order is of *irregular structure*. Chain irregularity may be due to different reasons.

First of all, chain irregularity may be a result of identical repeating units following each other in the chain in different positions. For example, in a polymerization reaction repeating units

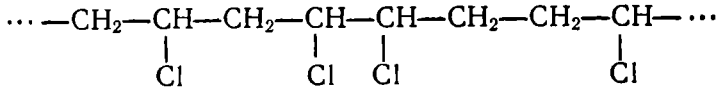
may combine according to scheme I or scheme II:



(I)

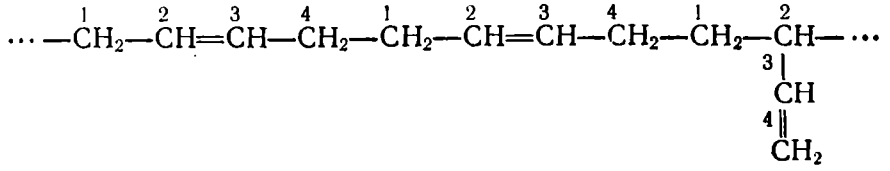
(II)

Addition according to the former scheme is called "head-to-tail", and that according to the latter scheme — "head-to-head" or "tail-to-tail". In most polymerizations, monomers combine according to the "head-to-tail" scheme, but some monomers may add according to scheme II in some sections of the chain, disturbing the regularity of the latter. Such a chain irregularity occurs, for example, in poly(vinyl chloride):



polystyrene and other vinyl polymers.

Chain irregularity due to different ways of monomer addition (1,4- and 1,2-) is also observed in polyenes:



Secondly, chain irregularity may be caused by different degrees of branching, since the sites of addition of the side chains, the number of branches, and their lengths may differ. Branched polymers are very irregular in structure.

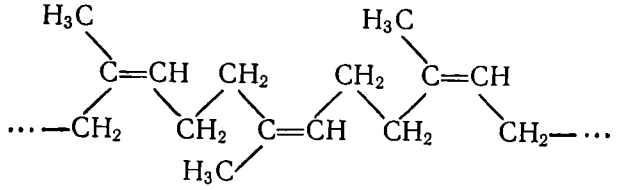
Thirdly, chain irregularity may be a result of random alternation of monomers of different chemical constitution. This type of irregularity is observed mostly in copolymers, because on copolymerization the monomer residues may combine randomly.

Stereoregularity in polymers is very important.

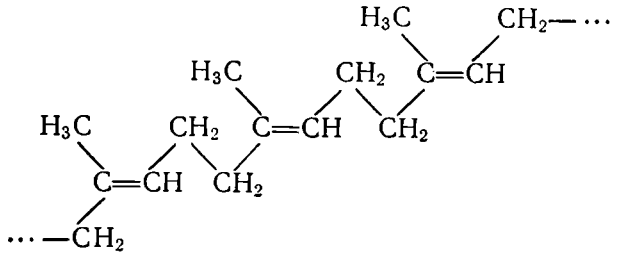
Stereoregular polymers are polymers in which all units and substituents are arranged in space in some definite order. A polymer lacking such order of spatial arrangement is said to be *stereoirregular.* Differences in spatial arrangement of units or substituents give rise to configurational isomerism of polymers which includes *cis-trans* and *D-L* isomerism.

Cis-trans isomerism is found in polymers containing double bonds in their main chains. In the *cis*-isomers the carbon atom chains are all on the same side of the plane of each double bond,

whereas in the *trans*-isomers they are alternately on one and on the other side, e.g.,



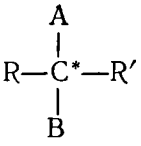
cis-isomer (natural rubber)



trans-isomer (gutta-percha)

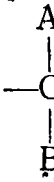
Both compounds are stereoregular. A polymer, in which the diene residues in the chain are connected randomly in the *cis*- and *trans*-positions, is stereoirregular.

The second type of configurational isomerism is *D-L isomerism*, which is due to the presence of an asymmetric carbon atom in the polymer chain:



The asymmetry is determined by unequal length and possible differences in space configuration of the two parts of the molecular chains connected to each carbon atom ($R \neq R'$), in the presence of two different substituents A and B. Polymers in which all adjacent asymmetric carbon atoms over the length of at least one macromolecular chain have the same space configuration are called *isotactic polymers*. Polymers whose macromolecules are made up of units with opposite space configuration of each consequent asymmetric carbon atom in the chain are called *syndiotactic polymers*.

Isotactic and syndiotactic polymers can be defined otherwise. In the wide sense of the word, isotactic structure is characterized by periodic repetition in the main chain of adjacent or separated



groups, where $A \neq B$. The substituents A and B are arran-

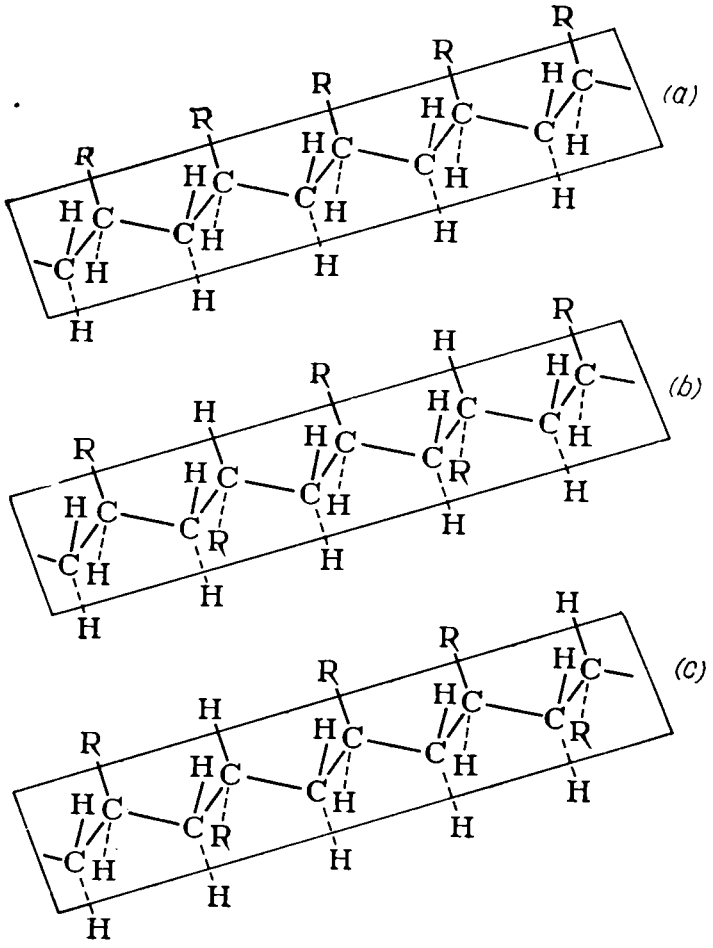
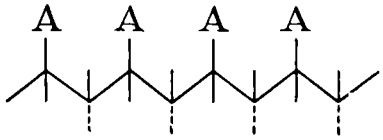
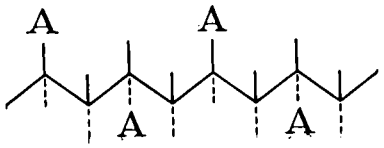


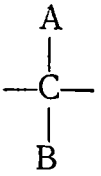
Fig. 1.2. Isotactic (*a*), syndiotactic (*b*), and atactic (*c*) polyolefins

ged in space so that on moving along the chain they will coincide if the skeleton carbon atoms of two contiguous units of the chain are superimposed:



In syndiotactic structure the substituents of contiguous units do not coincide, but those of units with one unit of opposite space configuration between them, do:



Polymers with their  groups arranged irregularly in space are called *atactic*. Figure 1.2 is a schematic representation of molecules of isotactic, syndiotactic, and atactic polyolefins.

1.3.2. Chemical Heterogeneity

Chemically heterogeneous polymers are polymers that contain units of different composition in the same chain. For example, some of the units may be completely esterified, while others contain free hydroxyl groups. Commercial-grade cellulose esters, poly(vinyl alcohol) and some other commercial polymers are chemically heterogeneous. The chemical composition of such polymers is conventionally characterized by the average percentage content of functional (e.g., acetyl) groups in them, by their nitrogen content, etc.

The content of acetyl groups in cellulose triacetate, expressed by the ratio $\frac{M_{OCOCH_3}}{M_u}$, is 61.5 per cent. The more common cellulose acetates of commerce contain 54 to 58 per cent $OCOCH_3$ groups. With such an average composition the number of acetylated hydroxyl groups in different units may vary considerably.

The theoretical nitrogen content of cellulose trinitrate is 14 per cent. The cellulose nitrates used in practice average from 10 to 13.5 per cent nitrogen (with different numbers of nitrate groups in different units).

1.3.3. Molecular-Mass Heterogeneity. Polymolecularity *

As was said above, the most characteristic feature of polymeric compounds is their high molecular mass, i.e., the very large size of their molecules. However, there are practically no polymers whose molecules are all strictly of the same size or, in other words, have the same degree of polymerization. Alongside very large molecules a polymer may also contain relatively small ones (molecular mass of the order of 1000) and molecules of intermediate size. Hence, all polymers are more or less heterogeneous with respect to molecular mass and are said to be *polymolecular*. That is why polymer chemistry uses the concept *average molecular mass* (p. 498). A series of polymeric compounds of the same chemical structure differing only in molecular mass is known as a *polymer-homologous series*.

* Also called *polydispersity*.

1.3.4. Polar and Nonpolar Polymers

A chemical bond may be polar or nonpolar. The extreme polar bond is the ionic one, i.e., the bond formed by separate charges, as in the molecule Na^+Cl^-. The extreme nonpolar bond is the covalent bond formed by identical atoms, as in the molecules H_2, O_2, and Cl_2. In the former case an electron passes from one atom to the other; in the latter the electron cloud becomes perfectly symmetrical relative to the nuclei of both atoms. All other bonds are intermediate between these two. Thus, the covalent bond formed by dissimilar atoms, e.g., HCl or HF, is polar, because the probability of the bonding electrons being in the field of the nuclei of the different atoms is unequal, since the atoms differ in electron affinity. The electron affinity of chlorine is greater than that of hydrogen, and therefore the average density of the electron cloud around the chlorine atom is higher than around the hydrogen atom. As a result, the molecule acquires a definite electrical or *dipole moment* μ_0, numerically equal to the product of the electric charge q and the distance between the charges l:

$$\mu_0 = ql$$

The distance between charges is approximately 10^{-8} cm, and the charges are about 10^{-10} electrostatic units each. Hence, the dipole moments of molecules are of the order of $10^{-8} \times 10^{-10} = 10^{-18}$ esu cm (1 debye). Dipole moments range from zero to 10 debyes.

The dipole moments of symmetrical molecules (H_2, Cl_2, CH_4, C_2H_6, etc.) are zero ($\mu_0 = 0$). All aliphatic hydrocarbons possess symmetrical structure and their dipole moments are therefore zero (*nonpolar* molecules). The water molecule is asymmetrical and is said to be dipolar or *polar*. Its dipole moment is 1.84 D.

In the bonds C—OH, C—COOH, C—NH_2, C—Cl, and C—F electron density is distributed unsymmetrically and these are called *polar bonds*. Introduction of such polar bonds into the molecule imparts a dipole moment to the compound (unless the bonds neutralize each other).

Polymeric hydrocarbons are nonpolar. These include: polyethylene, polypropylene, polybutadiene, polyisoprene, and polyisobutylene. Among the most polar polymers are poly(vinyl alcohol), cellulose, and starch, which contain a large number of polar OH groups, polyacrylonitrile, which contains a large number of highly polar CN groups, poly(acrylic acid) and poly(methacrylic acid) (COOH groups). Poly(vinyl chloride), with its C—Cl bonds, and cellulose acetate and nitrate (with $OCOCH_3$ and ONO_2 groups) are of intermediate polarity. Still less polar are polymeric esters (e.g., polyacrylates and polymethacrylates).

However, the presence of polar groups in a molecule does not

always make it polar as a whole. If the polar bonds in the molecule are arranged symmetrically, their electric fields neutralize each other and the dipole moment of the molecule equals zero. Carbon tetrachloride contains polar C—Cl bonds, but they are arranged symmetrically, and therefore $\mu_0 = 0$. The same can be said of some polymers. For example, the C—F bond is polar, but in polytetrafluoroethylene these bonds are arranged symmetrically; therefore, the electric field of the unit is symmetrical, and the macromolecule as a whole is nonpolar, in spite of a large number of C—F bonds.

Thus, the polarity of a polymer can be judged from the polarity of its constituent groups, with allowance for the symmetry of spatial arrangement of these groups and for the frequency of their occurrence along the chain (Chap. 11).

1.3.5. Principal Characteristics of Polymer Structure. Polymeric State of Substances

Table 1.4 gives only the most typical polymer substances. In reality, there are very many of them. What unites them?

The main structural feature of a polymeric compound is the presence in it of chain molecules in which a large number of atoms are combined consecutively. It has two kinds of bonds, chemical and intermolecular, which differ greatly in energy and length. The atoms in the chain are joined to each other by strong chemical bonds about 1-1.5 Å in length. Much weaker intermolecular forces interact between the chains at distances of about 3-4 Å (see Chap. 4). Crosslinked (three-dimensional) polymers have chemical bonds (crosslinks) between their chains. If the number of crosslinks is much smaller than the number of bonds between the atoms in the chain or, which is the same, if the chain lengths between the nodes of the spatial network are sufficiently large, the compound retains the properties of a polymer. If the atoms are connected by chemical bonds only, as in diamond, where each carbon atom is joined by covalent chemical bonds with four other carbon atoms situated 1.5 Å away from it, the substance will not possess typical "polymeric" properties. Evidently such limiting types of three-dimensional crystalline and even noncrystalline structures should not normally be classed as polymers. They are ordinary solids without polymeric properties.

Such inorganic compounds as *boron carbide* B_4C, calcined aluminium oxide (*corundum*) Al_2O_3, and silicon carbide (*carborundum*) SiC should not be classed as polymers. These are substances with high melting points (2000-2600 °C) close in structure and properties to diamond and are therefore ordinary crystalline solids.

The structure characteristic of graphite and many inorganic compounds is a crystalline lamellar lattice in which the bond energy between the atoms in the same plane differs considerably from that between the atoms in different planes. Therefore compounds with graphite-like structure may be considered polymeric compounds. They include graphite and silicon carbide.

The presence of large macromolecules and two types of bonds predetermines all properties which are typical of polymers and which are not possessed by low-molecular substances; these properties will be discussed in the following chapters.

Since all elements except univalent ones may form polymeric compounds, any substance in principle may be transferred to a *polymeric state.*

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CHAPTER 2

Synthesis of Polymers

Synthetic polymers are produced from low-molecular compounds by polymerization and polycondensation reactions, as well as by chemical transformation of other natural and synthetic polymers (see p. 82).

2.1. POLYMERIZATION

Polymerization is the reaction of linking together of several molecules (monomers), not accompanied by the formation of by-products and involving no change in elementary composition.

Distinction is made between chain and step polymerizations.

2.1.1. Chain Polymerization

The theory of *chain polymerization* was developed by S. Medvedev and other workers on the basis of N. Semenov's theory of chain reactions.

Chain polymerization is characteristic of compounds with multiple bonds [e. g., ethylene $CH_2=CH_2$, isobutylene $(CH_3)_2C=CH_2$, and vinyl chloride $CH_2=CHCl$], or of unstable rings containing hetero-atoms (e.g., ethylene oxide $CH_2—CH_2$, with O bridging the two carbons).

The specific feature of chain polymerization reactions is that development of the kinetic chain is accompanied by growth of the molecular chain.

The chain polymerization reaction consists of three main steps:

1. Activation, or initiation, of the monomer molecule:

$$M \longrightarrow M^*$$ (excited monomer molecule or active centre)

2. Chain propagation:

$$M^* + M \longrightarrow M_1^*$$
$$M_1^* + M \longrightarrow M_2^*$$
$$M_2^* + M \longrightarrow M_3^*$$
$$\cdots\cdots\cdots$$
$$M_{n-1}^* + M \longrightarrow M_n^* \text{ (activated growing polymer molecule)}$$

3. Chain termination:

$$M_n^* \longrightarrow M_n \text{ (unactivated polymer molecule)}$$

The active centre in chain polymerization reactions may be a free radical or an ion, and the reaction is one of radical or ionic polymerization, respectively.

2.1.1.1. Radical Polymerization

In *radical polymerization* physical or chemical effects give rise to a free radical:

$$M \longrightarrow R\bullet$$

This primary free radical reacts with the double bond of an unexcited monomer molecule and adds to it, forming a new radical capable of further interaction with the initial monomers (chain propagation):

$$R\bullet + M \longrightarrow R{-}M\bullet$$
$$R{-}M\bullet + M \longrightarrow R{-}M{-}M\bullet$$
$$\cdots\cdots\cdots\cdots$$
$$R{-}M{-}M\bullet + nM \longrightarrow R{-}M_{n+1}{-}M\bullet$$

The resulting macroradical may change into an inactive polymer molecule (chain termination) in the following ways:

(a) recombination of primary radicals

$$R\bullet + R\bullet \longrightarrow R{-}R$$

(b) combination of macroradicals

$$R_{n-1}{-}M\bullet + R_{m-1}{-}M\bullet \longrightarrow P_{n+m}$$

(c) combination of a macroradical with a primary radical

$$R_{n-1}{-}M\bullet + R_m\bullet \longrightarrow P_{n+m}$$

(d) disproportionation.

Methods of Initiation. Activation of a monomer to transform it into a primary radical requires the application of energy. This process can be brought about by the action of heat, light, or an ionizing radiation (α-, β-, or γ-rays) or by adding to the system extraneous free radicals or substances (initiators) that break down readily into free radicals. Depending on the method of formation

of free radicals the polymerization is said to be thermally, photochemically, radiation, or chemically initiated.

Thermally initiated polymerization is a polymerization wherein the monomer molecule is activated by heat. This is a very important method because in practice polymerization very often involves heating. However, in the pure form thermal polymerization is not very probable; it is usually accompanied by polymerization under the action of catalysts or initiators.

Photochemical polymerization is a polymerization in which the molecule is activated as a result of the absorption of luminous energy. Photochemical polymerization may occur at temperatures whereat polymerization initiated by other methods does not proceed.

In *radiation polymerization* the molecule is activated (free radicals are formed) by the action of ionizing radiations. The process proceeds subsequently by a radical mechanism.

Chemically initiated polymerization, one of the most widely used methods, consists in activating the monomer molecules by substances capable of decomposing into free radicals when heated. Such substances include inorganic and organic peroxides (hydrogen peroxide, benzoyl peroxide), hydroperoxides, and diazo compounds. The widely used initiator benzoyl peroxide decomposes readily when heated into two free radicals:

$$C_6H_5COO—O—COC_6H_5 \longrightarrow C_6H_5\bullet + C_6H_5COO\bullet + CO_2$$

These radicals serve as active centres; they cause chain propagation by combining with monomers:

$$C_6H_5COO\bullet + CH_2{=}\underset{\displaystyle X}{\underset{|}{CH}} \longrightarrow C_6H_5COO—CH_2—\underset{\displaystyle X}{\underset{|}{CH}}\bullet$$

$$C_6H_5—COOCH_2—\underset{\displaystyle X}{\underset{|}{CH}}\bullet + CH_2{=}\underset{\displaystyle X}{\underset{|}{CH}} \longrightarrow C_6H_5COOCH_2—\underset{\displaystyle X}{\underset{|}{CH}}—CH_2—\underset{\displaystyle X}{\underset{|}{CH}}\bullet$$

In this case the initiator molecule residues form part of the growing polymer chain.

Oxidation-reduction initiation is often used in polymerization. Here free radicals formed as a result of an oxidation-reduction reaction initiate the polymerization, e.g.,

$$ROOH + Fe^{2+} \longrightarrow RO\bullet + OH^- + Fe^{3+}$$

Oxidation-reduction reactions require much less activation energy than the thermal decomposition of peroxides to free radicals (approx. 10 kcal/mole as compared to 30-35 kcal/mole). This makes it possible to carry out the polymerization at lower temperatures.

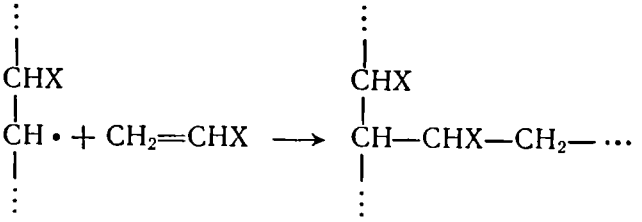
Chain Propagation. Chain propagation and termination reactions do not depend on the method of activation of monomer. Polymer chain propagation is accomplished by addition of monomer molecules to free radicals (formation of macroradicals). The chain propagation reaction determines the rate of the polymerization, the molecular mass of polymer, the structure of the polymer chain, i.e., the mode of monomer addition ("head-to-tail" or "head-to-head"), the degree of branching, etc.

Chain polymerization reactions may be accompanied by chain transfer and by reactions of macroradicals with double bonds in the polymer chain. *Chain transfer* consists in interaction of a growing polymer radical with a saturated molecule AB, resulting in termination of the molecular chain

$$R{-}CH_2{-}CHX\bullet + AB \longrightarrow R{-}CH_2{-}CHX{-}A + B\bullet$$

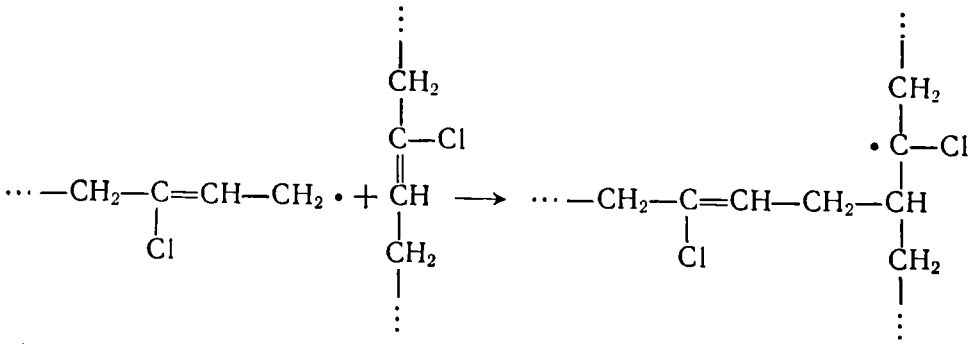
with the simultaneous formation of a new radical B·, which starts a new chain.

Chain transfer reactions usually involve the interaction of active centres with monomer, polymer, or solvent molecules. The new active centre may form in the middle of the chain and cause branching:



Chain transfer reactions account, for instance, for the formation of branched products upon radical polymerization of ethylene.

Of great importance in the polymerization of diene compounds is interaction of the polymeric radical with a double bond:



This reaction results in highly branched polymers, and their numerous repetitions will give network structures.

Chain Termination. Chain termination results from saturation (deactivation) of the macroradical and may occur by combination of free radicals, disproportionation or chain transfer.

Combination consists in the mutual saturation of two macroradicals or of a macroradical and a low-molecular free radical:

$$R{-}CH_2{-}CHX{-}\cdots{-}CH_2{-}CHX\bullet + \bullet CHX{-}CH_2{-}\cdots CHX{-}CH_2{-}R' \longrightarrow$$
$$\longrightarrow R{-}CH_2{-}CHX{-}\cdots{-}CH_2{-}CHX{-}CHX{-}CH_2{-}\cdots{-}CHX{-}CH_2{-}R'$$

Disproportionation is the transfer of a hydrogen atom of one macroradical to another to form two macromolecules, one of them with a double bond at its end:

$$R{-}CH_2{-}CHX{-}\cdots{-}\overset{\downarrow}{C}H_2{-}CHX\bullet + \bullet CHX{-}CH_2{-}\cdots{-}CHX{-}CH_2{-}R' \longrightarrow$$
$$\longrightarrow R{-}CH_2{-}CHX{-}\cdots{-}CH{=}CHX + CH_2X{-}CH_2{-}\cdots CHX{-}CH_2{-}R'$$

Chemical substances capable of reacting with free radicals to terminate the reaction chain are called polymerization *inhibitors* (examples are hydroquinone and trinitrobenzene). Chemical compounds which are only chain-transfer agents, i.e., do not affect the rate of polymerization but determine the molecular mass of polymer, are called polymerization *regulators*, or *modifiers*. These substances are added to the reaction mixture in strictly rated amounts.

Purity of Initial Monomer. The rates of radical polymerization reactions and the properties of the resulting products are very sensitive to impurities in the monomer, which may act as initiators or inhibitors. Therefore to obtain a homogeneous high-quality polymer very pure monomers should be taken for the polymerization.

2.1.1.2. Ionic Polymerization

In *ionic polymerization* the active centres initiating the chain reaction are ions. Ionic polymerization proceeds in the presence of catalysts and is called catalytic polarization.

Depending on the charge of the ion formed, the polymerization may be cationic or anionic.

Cationic, or *carbonium*, *polymerization* involves the formation of a carbonium ion, this being a polar compound with a tricovalent carbon atom carrying a positive charge, $R{-}\overset{+}{C}H{-}R'$. Catalysts of carbonium polymerization are compounds with pronounced electron-acceptor properties (aluminium chloride, stannic chloride, titanium tetrachloride, boron fluoride, etc.), the polymerizing monomer being an electron donor (e.g., styrene in the presence of $SnCl_4$).

A carbonium ion interacts with a monomer molecule, the reaction of chain growth being accompanied with the communication of a positive charge along the chain. Consequently, the growing

chain itself is a cation with a molecular mass increasing in the course of polymerization. The pattern of the growing chain of polystyrene, being polymerized in the presence of $SnCl_4$, is given below:

$$[SnCl_4]^-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-\cdots-CH_2-\overset{+}{\underset{\underset{C_6H_5}{|}}{CH}}$$

Chain termination apparently occurs as a result of the mutual collision of the ends of a growing ion; in addition, the catalyst is split off. Hence, in cationic polymerization, the catalyst is not in the macromolecule.

Anionic, or *carbanion, polymerization* involves the formation of a carbanion, a compound with a trivalent carbon atom carrying a negative charge. Anionic polymerization occurs in the presence of catalysts which yield electrons readily, i.e., electron donors; examples are sodium or potassium amide, triphenylmethylsodium, alkali metals, alkylalkalis, etc. Polymerizations occur by the carbanion mechanism in the case of monomers containing electronegative substituents at one of the carbon atoms connected by a double bond; such monomers are acrylonitrile, methyl methacrylate, etc.

Potassium amide dissociates in a liquid ammonia medium:

$$KNH_2 \rightleftarrows K^+ + NH_2^-$$

and the anion NH_2^- is added to a monomer molecule. The chain growth reaction is always accompanied with a transfer of a negative charge along the chain; consequently, the growing chain is always an anion of growing size. Chain termination occurs as a result of the collision of a growing ion with a molecule of the medium, such as an ammonia molecule:

$$(NH_2)-\left(CH_2-\underset{\underset{R}{|}}{CH}\right)_n-CH_2-\overset{-}{C}HR + NH_3 \longrightarrow NH_2^- +$$

$$+ NH_2-\left(CH_2-\underset{\underset{R}{|}}{CH}\right)_n-CH_2-CH_2-R$$

Thus, every growing chain contains the NH_2 group.

Ionic polymerization may occur in the presence of more than one catalyst (*cocatalysts*), e.g., in the presence of alkyl metals and chlorides of metals of variable valency ($TiCl_3$, $TiCl_4$).

Anionic polymerization has great advantages, since spontaneous chain termination does not occur. Monomolecular polymers of a high molecular mass may be produced upon polymerization in the presence of metalorganic compounds and alkali metals and in the absence of impurities which are capable of causing chain ter-

mination. Anionic polymerization is an up-to-date method of producing monomolecular polymers.

In anionic polymerization, the end group of a growing macromolecule possesses high activity and great stability. Therefore, the polymers produced by this method retain active centres at the end of the chain; later, these centres are capable of initiating the polymerization of monomers. Such polymers are known as "*living polymers*". The process of polymerization occurs when a new portion of a monomer is added to such a living polymer. Such a method is used to produce, for example, block copolymers.

2.1.1.3. Stereospecific Polymerization

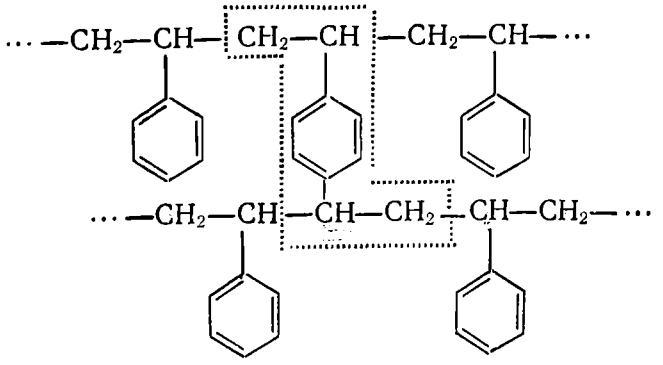
A *stereospecific polymerization* is one which results in stereoregular polymers. It may proceed by an ionic or a radical mechanism. Stereospecific polymerization was discovered by the Italian scientist Natta and is being successfully developed by Korotkov and Dolgoplosk.

2.1.1.4. Copolymerization

Copolymerization is a polymerization involving two or more monomers of different structures. The properties of polymers synthesized by copolymerization can be varied over a wide range by adjusting the monomer ratio. Besides, some unsaturated compounds, which are incapable of separate polymerization, polymerize readily together with other unsaturated compounds.

Copolymerization can be used to obtain polymers of linear, branched, and crosslinked structures. Thus, crosslinked polymers are formed if the molecule of one of the monomers contains two double bonds, even if the amount of monomer added is very small. Such monomers are called crosslinking agents. For example, if an insignificant amount of divinylbenzene

is added to styrene, they will copolymerize to form an insoluble, nonmelting copolymer of crosslinked structure:



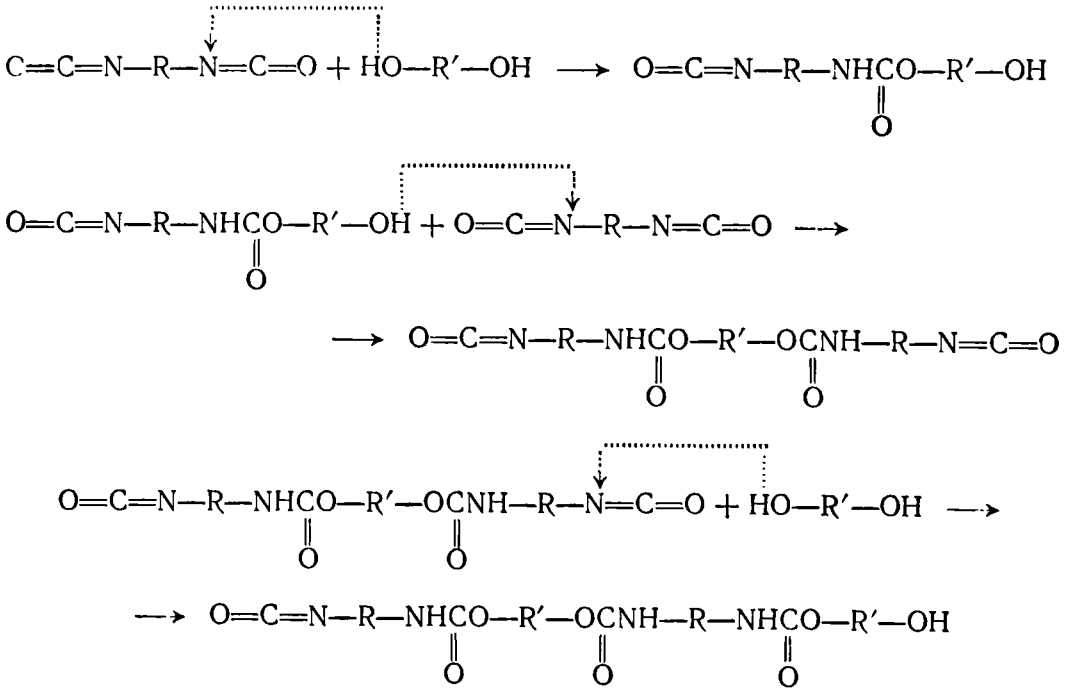
This material is used in practice for making ion exchange resins (see Chap. 20).

However, the formation of crosslinked polymers during polymerization may be undesirable. For instance, when preparing monovinylacetylene for chloroprene synthesis from acetylene, divinylacetylene $CH_2=CH-C\equiv C-CH=CH_2$ forms as a byproduct. Its presence in chloroprene polymerization causes the formation of a polychloroprene of crosslinked structure, which makes the polymer difficult to fabricate. Therefore, to obtain high-quality polychloroprene the monovinylacetylene must be thoroughly freed from impurities.

2.1.2. Step Polymerization

Step polymerization is the combination of several molecules by stepwise addition of monomer molecules to one another as a result of the migration of some mobile atom (mostly a hydrogen atom) from one molecule to another.

An example of step polymerization is the polymerization of diisocyanates and dihydric alcohols into linear polyurethanes:



etc.

The reaction of diisocyanates with trihydric alcohols (e.g., glycerol or trimethylolpropane) yields crosslinked polymers. Crosslinked polyurethanes also form in an excess of diisocyanate.

2.1.3. Polymerizability of Monomers and Thermodynamics of a Process

The *polymerizability* of a monomer depends mainly on the easiness of displacement of the electron cloud, i.e., on the polarizability of the double bond. The double bond is not polarized in symmetrically arranged molecules (ethylene, symmetrical butylene). Therefore, they polymerize with difficulty. The unsymmetrically introduced substituents promote the polarization of the double bond, and polymerization is facilitated. Therefore, propylene and isobutylene are polymerized easier. The degree of polarization increases upon an introduction of polar substituents ($CH_2=CH-$ $-C\equiv N$; $CH_2=CH-COOH$). The double bond in a styrene molecule is also polarized; therefore, styrene is polymerized easier than ethylene.

Nonpolar molecules, which themselves polymerize with difficulty, may polymerize under the influence of the polar molecules of another monomer. Therefore, a monomer itself may not polymerize, but it may copolymerize with another monomer.

The polarizability of a monomer affects only the initiation stage; the stage of growth depends on the activity of a free radical that is being formed. In some cases, the activity of a monomer and that of a radical do not coincide. Thus, the less is the conjugation effect in a monomer, the less active it is and the more active is the radical that is formed from it. The overall process of polymerization depends on the activity of the former and of the latter.

The possibility of polymerization of a monomer may be predicted on the basis of general thermodynamic consideration, according to which the process may occur spontaneously at constant temperature and pressure if it is accompanied with a reduction of free energy G (p. 371). It follows that the free energy of a polymer should be less than the free energy of a monomer. Let us examine this question at first by taking the example of polymerization of monomers with multiple bonds.

The process of the formation of long macromolecules from randomly arranged monomers always results in their ordering; consequently, the entropy of a polymer is less than the entropy of monomers, the process is accompanied with a decrease in entropy and, according to the equation $\Delta G = \Delta H - T\Delta S$, this does not promote the polymerization process. For the process to occur, it must be accompanied with a decrease in enthalpy and $|\Delta H|$ should be greater than $|T\Delta S|$.

Upon polymerization, the double bond breaks up and two ordinary bonds are formed. The energy of the bond C=C is 145.5 kcal/mole, and the energy of the bond C—C is 84 kcal/mole. Hence, 145.5 kcal/mole are consumed, and $2 \times 84 = 168$ kcal/mole

are saved. The difference, 22.5 kcal/mole, is the enthalpy of polymerization. It follows that polymerization is an exothermal reaction. However, upon polymerization of most monomers, less than 22.5 kcal/mole are lost. This is connected with the losses of conjugation energy, the interaction of side groups, and so forth. Nevertheless, the polymerization process occurs if the absolute value of ΔH is greater than that of $T\Delta S$, which is usually 7-10 kcal/mol. If this is not so, the monomer will not polymerize.

Let us consider the thermodynamics of polymerization of ring compounds. The lower rings are known to be strained. The strain energy decreases as the number of carbon atoms in the ring increases. Six-membered rings are virtually not strained, and strain again grows with a subsequent increase in the number of carbon atoms.

When nonstrained cycles are opened, the bonds do not change, and consequently $\Delta H \cong 0$. The process occurs only owing to a change in entropy. Entropy depends on the number of degrees of freedom. When molecules are connected into a ring, a loss in the number of degrees of freedom occurs. Consequently, the process of ring formation is accompanied with a decrease in entropy, and the process of its opening is accompanied with its increase. When the ring is opened, $\Delta S = 2.5$ kcal/mole. Since $\Delta H \cong 0$, then $\Delta G > 0$. Hence, the process of polymerization of the nonstrained rings is thermodynamically disadvantageous.

However, if the rings are strained, their enthalpy is higher than that of an extended chain, and the opening of a ring is accompanied with the heat generation. Consequently, $\Delta G < 0$. The values of ΔH and ΔG for different rings are given below.

Number of carbon atoms in a ring	ΔH	ΔG
3	−27.0	−22.1
4	−25.1	−21.5
5	−5.2	−2.2
6	+0.7	+1.4
7	−5.2	−4.9
8	−8.3	−11.0

It follows that three- and four-membered rings and rings with a larger number of carbon atoms are easily polymerized.

2.1.4. Effect of Various Factors on Polymerization Rate

Effect of Temperature. In radical polymerization the rate of reaction usually increases with rising temperature.

Changing the temperature also affects the structure of the resulting products. Thus, in butadiene polymerization raising the temperature will cause ring dimers to form instead of chain molecules. That is why butadiene is polymerized at temperatures not

over 60 °C. However, even below this temperature the size and structure of the chains depend on temperature. It has been established that at lower temperatures most monomers form polymers of higher molecular mass. For instance, high-molecular products can be obtained from isobutylene only at —80 °C, and from α-methylstyrene, at —130 °C.

Raising the temperature increases the degree of branching of a polymer.

Effect of Pressure. Raising the pressure considerably increases the rate of polymerization, because this increases the number of collisions between active centres and monomers. Raising the pressure enables a lower temperature of polymerization, and hence the production of polymers with higher molecular masses. Butadiene polymerization takes 46 hours (95 per cent conversion) at 7000 atm and 48 °C, and only 19 hours at the same pressure and 61 °C, but at 1 atm it takes hundreds of days (in the absence of catalysts). However, the use of elevated pressures for polymerization should always be considered in conjunction with the choice of a catalyst. Thus, polyethylene, which could be produced formerly only at a pressure of 1000-2000 atm (high-pressure polyethylene), can now be obtained by the Ziegler method involving the use of triethylaluminium and titanium chlorides as catalysts at a low pressure (low-pressure polyethylene).

2.1.5. Types of Polymerization

Several types of polymerization are known:

1. Gas-phase polymerization.
2. Bulk or mass polymerization.
3. Solution polymerization.
4. Emulsion polymerization.
5. Solid-phase polymerization.

Gas-Phase Polymerization. *Gas-phase polymerization* is a process carried out with the monomer in the gaseous state. Polymer formation begins on the walls of the reaction vessel and occurs on the surface or in the bulk of the particles of already formed polymer. Gas-phase polymerization is used, in particular, for the production of butadiene-sodium rubber.

Bulk Polymerization. *Bulk polymerization* is carried out in the liquid monomer at definite pressure and temperature. If the resulting polymer is soluble in a monomer, the viscosity of the medium increases gradually in the course of polymerization, and the result is a monolithic block of polymer. If the polymer is insoluble in a monomer, the polymer is obtained as a powder or a porous body.

Bulk polymerization can be used to produce polybutadiene, polystyrene, polychloroprene, poly(methyl methacrylate), and other

polymers. An essential disadvantage of the method is poor heat exchange in the system. Since polymerization is a highly exothermic process, this leads to considerable local overheating of the product, and the net result is a polymer of nonuniform molecular mass distribution. Besides, in bulk polymerization the monomer is not converted completely to polymer and the presence of a monomer is detrimental to polymer properties.

Solution Polymerization. In *solution polymerization* the reaction medium is a suitable solvent (usually organic); besides, initiators and modifiers are added. Two versions are possible:

1. Both monomer and polymer are soluble in the solvent. Polymerization results in a solution of polymer, called a lacquer, for which reason the method is known as the "lacquer method". This lacquer may be used directly for coatings or the polymer may be precipitated out of the solution.

2. A monomer is soluble in the liquid, but a polymer is not. In this case the polymer precipitates out as it is formed, and is then separated from the liquid.

Solution polymerization results in polymers of a lower molecular mass, but has a number of advantages over bulk polymerization: intensive stirring considerably improves heat exchange, and for this reason the resulting polymer is more uniform in a molecular mass; besides, it is much easier to remove it from a monomer.

The formation of polymers of lower molecular mass is due to chain transfer through solvent molecules if the latter contain mobile atoms or atomic groupings. This gives rise mainly to radicals of low activity, which are incapable of initiating a new chain. Collision of the radicals leads to chain termination, resulting in lower molecular mass of a polymer. The rate of chain transfer can be increased considerably by selecting suitable solvents and reaction conditions (temperature, pressure, monomer concentration, and nature and concentration of initiator), and this may result in polymers with degrees of polymerization ranging from 2 to 15.

This method of synthesis is called *telomerization*, and substances readily capable of chain transfer are called *telogens*.

Emulsion Polymerization. In *emulsion polymerization* the liquid monomer is dispersed in a liquid with which it does not mix to form an emulsion. The usual dispersion medium is water. Emulsions are thermodynamically unstable, and when they are concentrated emulsifiers must be added. *Emulsifiers* are surface-active agents that adsorb at the water-monomer interface. Essentially, the function of the emulsifier is to form mechanically stable adsorption layers which prevent merging (coalescence) of monomer or polymer droplets. Hence, the substances used as emulsifiers

usually contain a polar group and a comparatively large hydrocarbon radical. Examples are soaps (salts of higher organic acids), and organic sulphonic acids and their salts.

Polymer emulsions in water resulting from emulsion polymerization are called *synthetic latexes*. The latexes are used as such or the polymer is removed from them by the usual methods of coagulating colloidal systems. In practice latexes are coagulated by various electrolytes.

Solid-Phase Polymerization. Many monomers are capable of polymerizing not only in the liquid phase, but also in the crystalline state, below their melting points. Such polymerization is initiated by irradiating the monomer crystals with X- or γ-rays, fast electrons, or other high-energy particles. The crystal lattice of a monomer may affect the rate of chain propagation, the structure of the resulting macromolecules, and their packing.

On approaching the melting point (even if it is very low) the rate of polymerization of a solid monomer increases sharply and often turns out to be higher than the rate of polymerization of the same monomer in the liquid phase at considerably higher temperatures. It is thought that this is due to the formation near the melting point of so-called "labile blanks" in the crystals, these being groups of monomer molecules possessing fairly high mobility but preserving their ordered mutual arrangement. The combination of the two latter properties favours rapid chain propagation in the blanks.

In some cases the monomer crystals change on polymerization directly into bundles of highly oriented polymeric fibres (e.g., crystalline trioxane).

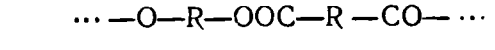
2.2. POLYCONDENSATION

Polycondensation is the combination of several molecules of like or unlike structure, accompanied, as a rule, by the formation of simple low-molecular substances. The initial monomers must contain at least two functional groups (OH, COOH, NH_2, etc.) in their molecule. The functionality of the initial compounds has a great effect on the structure and properties of the resulting polymers. Thus, monofunctional compounds yield only low-molecular products. Polycondensation of bifunctional compounds results in linear or cyclic high-molecular products, while tri- and tetrafunctional compounds give polymers of three-dimensional structure.

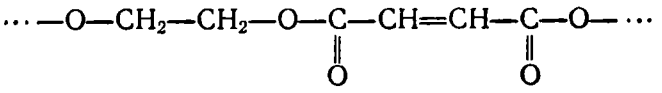
Polycondensation of dihydric alcohols results in linear polyethers:

$$n\text{HO—R—OH} + m\text{HO—R'—OH} \longrightarrow \cdots\text{—R—O—R'—O—}\cdots$$

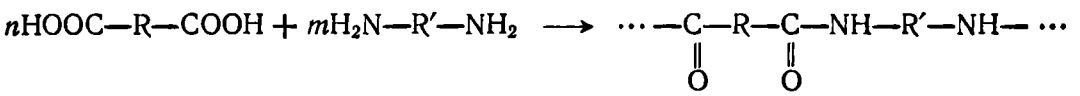
Dihydric alcohols react with dicarboxylic acids to form polyesters of the general formula



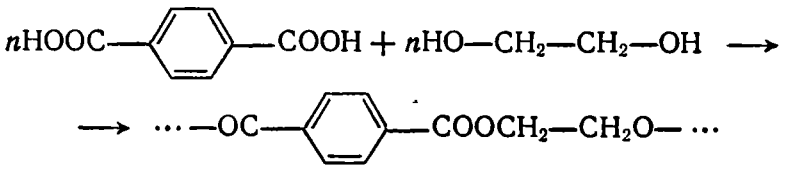
Of great practical importance are the unsaturated polyesters formed by polycondensation of dihydric alcohols with unsaturated acids or their anhydrides, e.g., with maleic anhydride:



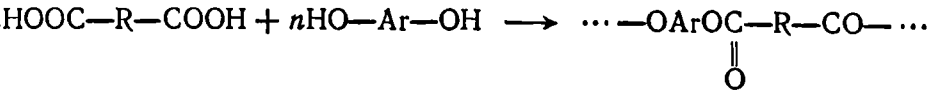
Polycondensation of dicarboxylic acids with diamines results in polyamides:



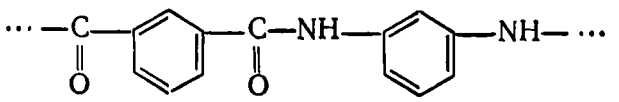
Lately aromatic compounds have come into frequent use for polycondensation reactions. For example, the polycondensation of ethylene glycol with terephthalic acid results in poly(ethylene terephthalate):



The polycondensation of dicarboxylic acids with aromatic dihydric phenols, such as hydroquinone, resorcinol, or phenolphthalein, gives *polyarylates*:

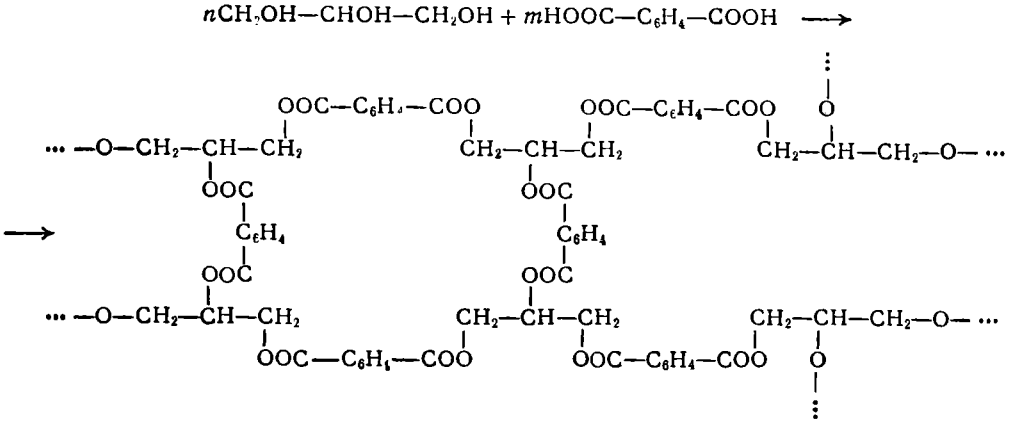


Polycondensation of dicarboxylic aromatic acids with aromatic diamines gives heat-resistant fibre-forming polymers. For instance, when isophthalic acid chloride is polycondensed with m-phenylenediamine, a polymer called *polyphenylone* is formed:

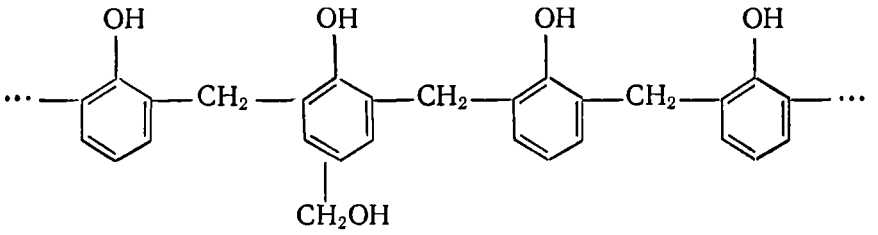


Polycondensation of compounds with a functionality of three and more with the addition of special reagents (hardeners) to form chemical crosslinks results in polymers of three-dimensional

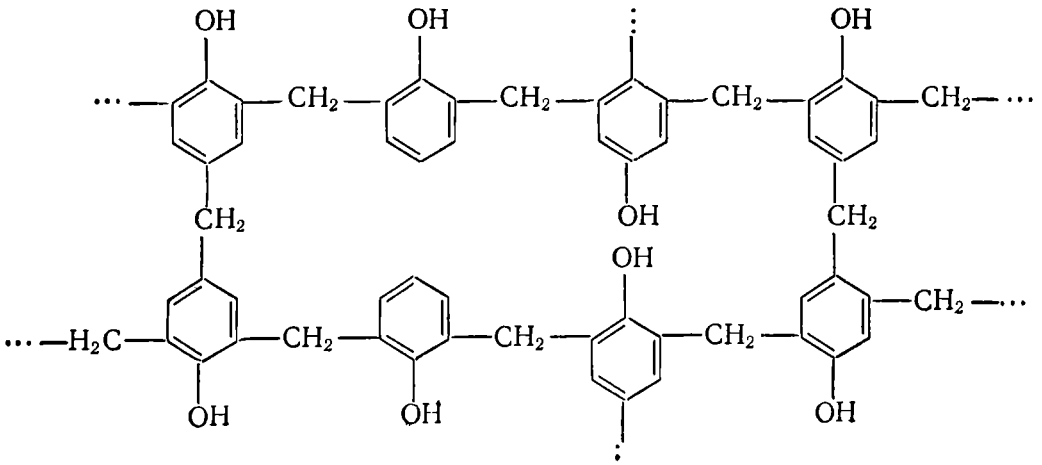
structure. A typical example of polycondensation of trihydric alcohols with dicarboxylic acids is the polycondensation of glycerol and phthalic anhydride:



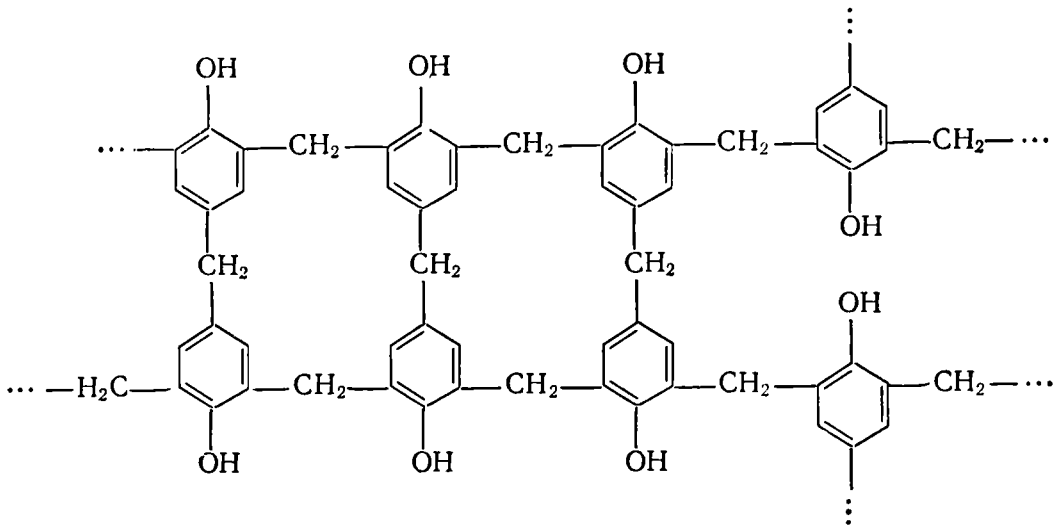
A classical example of the formation of a three-dimensional polymer is the polycondensation of phenols with aldehydes. The reaction of phenol with formaldehyde yields linear or branched low-molecular products, known as *resols*,



which change readily on further heating into *resitols*, three-dimensional polymers of low crosslink density:



The final stage of the process is the formation of *resites*, polymers of high network density:



Urea-aldehyde and melamine-aldehyde polymers are formed by similar reactions.

2.2.1. Basic Regularities of Polycondensation

Polycondensation is a reversible reaction. This means that two processes take place simultaneously, namely formation of the condensation products and their degradation.

Degradation (see Chap. 3) may be caused by the functional groups of the initial monomers, or be due to interaction of the condensation product with the low-molecular reaction byproduct (H_2O, HCl, etc.).

Owing to the reversibility of the polycondensation process equilibrium is reached at certain conditions corresponding to the formation of a polymer product of a definite molecular mass.

As a rule, polycondensation products have lower molecular masses (20 000-50 000) than polymerization products.

To obtain polymers of a higher molecular mass it is necessary, first of all, to remove the byproducts from the system, and, secondly, to use strictly equivalent ratios of functional groups (i.e., initial substances). An excess of one of the reactants always results in the formation of low-molecular products. For instance, when phenol or cresol reacts with aldehydes in a 10-fold excess of phenol, the only product formed is dihydroxyphenylmethane (no high-molecular products result). Figure 2.1 illustrates the effect of an excess of reaction components on the molecular mass of a polymer.

Polycondensation reactions can be carried out in the liquid monomer, in solution, in emulsion, in suspension, in the solid phase, or at the interface between two phases, in the absence or in the presence of catalysts.

If the initial components and the polymer are stable at the melting point, polycondensation is carried out in the melt at a

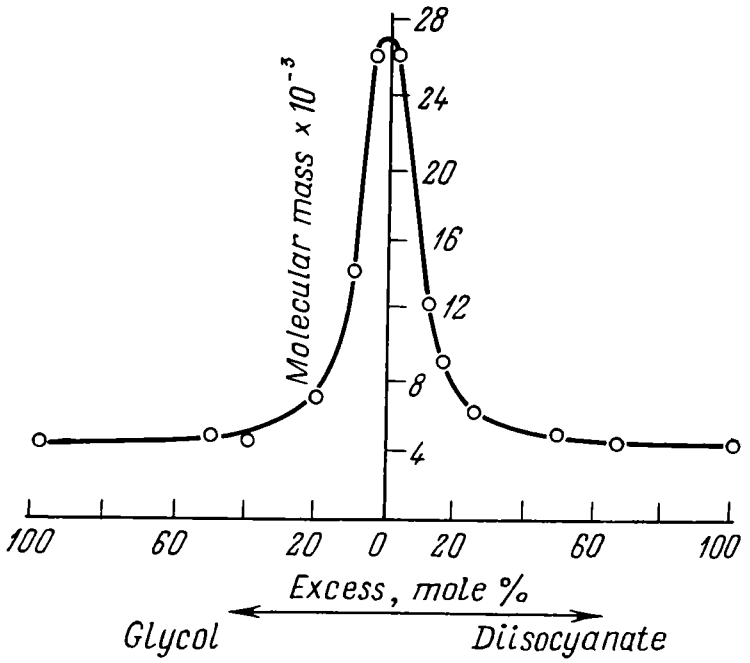


Fig. 2.1. Effect of excess of one of the components on molecular mass of polycondensation product

temperature of the order of 200-300 °C. To reduce the probability of side reactions taking place (oxidation, degradation, decarboxylation, etc.), the process is accomplished in an inert gas atmosphere and is usually completed under vacuum (for more complete removal of the byproduct).

To carry out polycondensation at the interface of two phases (*interfacial polycondensation*), the reactants are dissolved separately in two immixible liquids. As a rule, one of the liquids is water and the other, an organic substance. Usually one of the reactants is the dichloride of a dicarboxylic acid, and the other, a diamine, diol, etc. When the liquids come into contact, a polymer forms at the interface, while the byproduct dissolves in one of the liquids and is in this way removed from the reaction sphere. This makes interfacial polycondensation an irreversible process, so that equimolarity of the bifunctional substances is not necessary. By means

of interfacial polycondensation linear polymers can be obtained with high molecular masses (as high as 500 000). The polymer film formed at the interface is removed continuously. The rate of reaction is not high, but can be increased by stirring. This greatly increases the interfacial surface area between the polymer drops and the medium.

2.3. SYNTHESIS OF GRAFT AND BLOCK COPOLYMERS

The production of graft and block copolymers by direct copolymerization of two different monomers is difficult. To obtain them the initial substances must either be homopolymers of different chemical constitution or a homopolymer and a monomer differing in chemical composition from the monomeric unit of the homopolymer.

There are three groups of methods known at present for synthesizing graft and block copolymers.

1. Chain transfer through a polymer.
2. Activation of the polymer molecule.
3. Introduction of functional groups into the polymer.

The method of chain transfer to a polymer is based on the reaction of chain transfer discussed on p. 50. The reactants are the homopolymer and a monomer which polymerizes in its presence, e.g., poly(methyl methacrylate) and styrene. The growing polystyrene macroradical removes a hydrogen atom from the poly(methyl methacrylate) chain and is deactivated. This gives rise to an active centre (a carbon atom carrying an unpaired electron) in the poly(methyl methacrylate) chain and the polymerizing styrene chain is "grafted" onto this active centre. If the active centre (free radical) forms at the end of the chain, a block copolymer results. But if the active centre arises in the middle of the chain, the product is a graft copolymer.

Activation of the polymer molecule consists in forming an active centre in a homopolymer chain by some physical influence (thermal, mechanical, or luminous energy, or a high-energy radiation). This method will be discussed in detail in Chap. 3.

The third method consists in introducing groups into the homopolymer macromolecule, which will decompose readily when heated or irradiated to form free radicals, which initiate polymerization of the second monomer. The growing chain is then "grafted" onto the active centre of the homopolymer chain.

During the production of graft and block polymers the polymerizing monomer also forms a homopolymer, which can be removed from the copolymer if necessary.

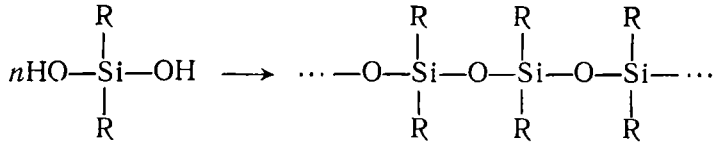
As distinct from copolymers obtained by usual methods, graft and block copolymers possess the properties of both homopolymers. Thus, the graft copolymer of starch and styrene possesses the properties of both starch and polystyrene. Block and graft copolymers are produced commercially, e.g., graft copolymers of acrylonitrile with cellulose and with natural rubber.

2.4. SYNTHESIS OF POLYMERS WITH INORGANIC MAIN CHAINS

Polymers with inorganic backbone chains, e.g., polyorganosiloxanes, polyorganometalsiloxanes, etc., are a very important class of elemento-organic polymers.

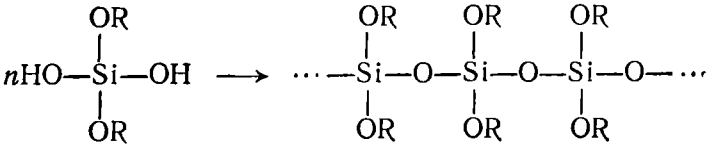
The methods of their production may differ from the methods usually employed for polymerization and polycondensation. Thus, polyorganosiloxane synthesis is based on hydrolysis of substituted halosilanes or esters of orthosilicic acid followed by polycondensation of the hydrolysis products — silanediols $R_2Si(OH)_2$ or silanetriols $RSi(OH)_3$.

Polycondensation of silanediols results in linear polymers of the following general structure:

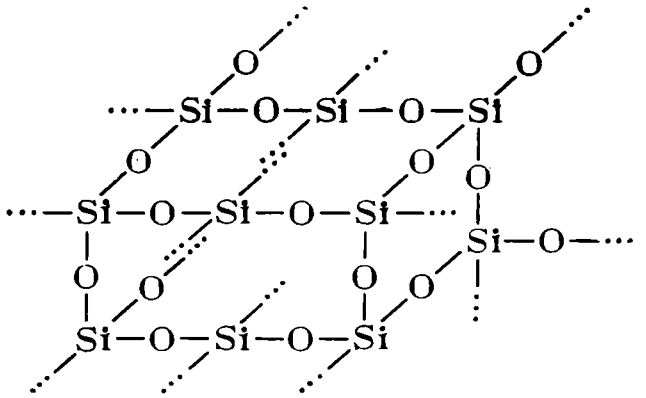


The Si—O—Si linkage is called a *siloxane bond.* The side-chain substituents may be any alkyl or aryl radicals.

Polymers whose main chains contain silicon atoms that form a chemical bond with organic radicals are called *siliconorganic polymers.* There are also high-molecular compounds in which organic radicals are joined to silicon atoms not directly, but through an oxygen atom. In particular, such polymers are obtained from aryl-substituted esters of orthosilicic acid of the general formula R_nSiX_{4-n}, where X is an OR group. These substances hydrolyze readily and enter into polycondensation reactions with the formation of siloxane bonds. Polycondensation of bifunctional compounds of this type also results in linear polymers:



Tri- or tetrafunctional derivatives of silicic acid form three-dimensional inorganic polymers:



The formation of polymers with inorganic backbone chains may be accompanied by ring formation. If polycondensation of organic monomers results, as a rule, in linear, branched, or three-dimensional polymers, the synthesis of polymers with inorganic main chains often gives ring polymers.

The ring structure of polyaluminosiloxanes has been proved by infrared spectroscopy and is confirmed by their ability to polymerize under the influence of catalists, opening the siloxane bonds in their ring molecules.

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CHAPTER 3

Chemical Transformations of Polymers

The following types of chemical reactions are distinguished in polymer chemistry:

1. Degradation.
2. Crosslinking.
3. Reactions between functional groups.
4. Intramolecular rearrangements.

In practice these reactions very often occur simultaneously.

3.1. DEGRADATION

Degradation is a reaction involving rupture of chemical bonds in the main chain of the macromolecule. Depending on the type of chemical bond (covalent or ionic), three mechanisms of polymer degradation are possible: radical, ionic, and iono-radical. If the bond between the atoms of the main chain is covalent, rupture of the macromolecules will involve the formation of free macroradicals *:

$$\cdots -CH_2-CH_2\vdots CH_2-CH_2-\cdots \longrightarrow \cdots -CH_2-CH_2\cdot + \cdot CH_2-CH_2-\cdots$$

Depending on the nature of the agent causing bond rupture in the chain, one distinguishes between physical and chemical degradation. *Physical degradation* falls into thermal, mechanical, photochemical, and ionizing-radiation degradation. *Chemical degradation* occurs under the action of various chemical agents. The most important types of chemical degradation are: oxidative degradation, hydrolysis, alcoholysis, acidolysis, and aminolysis.

* The presence of free radicals can be detected by electron paramagnetic resonance.

During the processing, and during service of articles made from them polymers are, as a rule, subject to the action of mechanical, thermal, radiation, and other kinds of influences simultaneously. In practice several different types of degradation reactions occur simultaneously. For example, very often a polymer is oxidized and heated at the same time (thermo-oxidative degradation); light catalyzes chemical degradation (photo-oxidative degradation), etc.

The macroradicals formed during degradation may enter into various reactions (p. 50), resulting in end products of linear, branched, or crosslinked structure. Free macroradicals may initiate a degradation reaction. For example, if the macroradicals formed on degradation of starch are added to undegraded starch, the latter will begin to degrade.

If the reaction occurs under conditions where the macroradicals formed are deactivated, the end product of degradation will be shorter chains, i.e., the molecular mass of polymer will decrease. Depending on the intensity and duration of action macroradicals of different length can be obtained, hence different degrees of degradation are possible.

Degradation resulting in elimination of a monomer is called *depolymerization.*

Degradation processes are of great practical importance because the properties of polymeric materials depend to a great extent on the length of their chains (i.e., on their molecular masses).

If the molecule of a low-molecular substance is split so as to divide its molecular mass in half, the result is obviously a new substance with properties differing sharply from those of the initial substance. But if a polymer is split similarly (e.g., so that its molecular mass decreases from 600 000 to 300 000), some of its properties will not be effected at all. A noticeable change in properties of a polymer is detected only if its molecular mass is decreased approximately tenfold, say, from 600 000 to 60 000.

Since polymers and polymeric materials are subject to various influences during processing and service, it is quite probable that the properties of the polymer will change sharply as a result of degradation. At the same time degradation is sometimes used purposely to obtain products with lower molecular masses. Hence, it is very important to know the mechanism and regularities of degradation processes to be able to keep them under control. Besides, degradation reactions are of great theoretical value for studying the structure of macromolecules.

Chemical transformations of polymers under the action of various agents are discussed below.

3.1.1. Effect of High Temperatures

When heated polymers undergo various chemical and physical changes accompanied by the formation of gaseous and liquid products, changes in colour, etc. We shall call the ability of a polymer to resist chemical decomposition at elevated temperatures its *thermal stability* *.

Thermal stability is usually assessed by the temperature at which noticeable decomposition of the polymer begins, by the decomposition products formed, and by the kinetics of the process.

The most important studies of the thermal decomposition of polymers are those of Grassie, Madorsky, Jellinek, Neuman, Kovarskaya, and other workers.

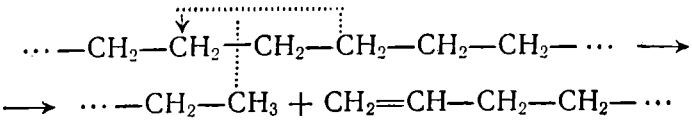
Chemical reactions of polymers at elevated temperatures fall into two main groups: reactions involving rupture of the main chain (degradation proper), and reactions proceeding without rupture of the main chain.

Reactions Involving Rupture of the Main Chain. When a polymer is heated, the energy of thermal motion at some points of the system, owing to thermal energy fluctuations **, becomes commensurable with the energy of a chemical bond and ruptures the bond. Obviously, a very important factor determining the thermal stability of a polymer is the energy of interatomic bonds in the main chain.

The carbon-carbon bond is one of the most resistant to thermal influences. This bond is especially stable in diamond. The presence of hydrogen atoms in the polymer molecule greatly decreases the energy of the C—C bond, and that is why high-molecular hydrocarbons and some of their derivatives possess comparatively low stability and are easily degraded by heating.

Rupture of the chemical bonds between carbon atoms may occur by two mechanisms:

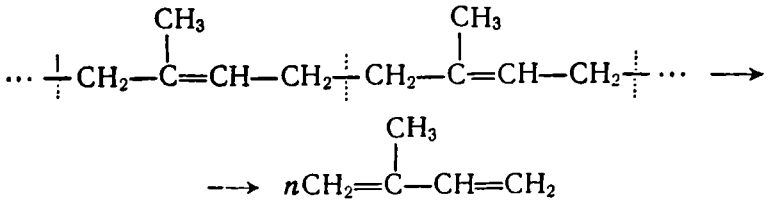
(1) intramolecular migration of hydrogen atoms, resulting in two chain fragments: one with a saturated end unit, and the other with an unsaturated one. These so-called random ruptures of chemical bonds are characteristic, for instance, of polyethylene:



* Note that we distinguish between thermal stability and heat resistance, the latter being the ability of the polymers to retain their hardness at elevated temperatures, on which the work capacity of articles made of them depends (p. 175).

** Fluctuations are statistical deviations from uniform distribution.

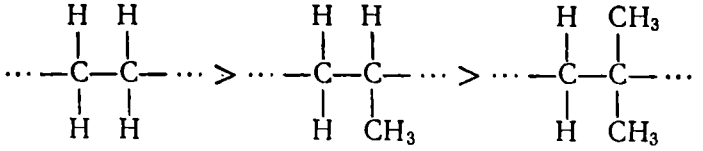
(2) chain rupture not at random points, but at the ends of the macromolecule, resulting in a monomer or products close in molecular mass to a monomer. This type of degradation is characteristic of polyene compounds, polystyrene, poly(methyl methacrylate), etc. For example, polyisoprene degrades to isoprene as follows:



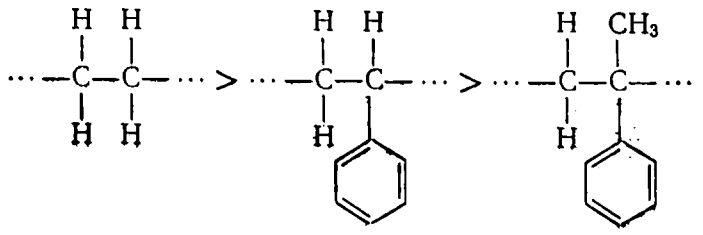
The probable mechanism of chain rupture is predetermined by the structure of the degrading polymer and by the process conditions. Thus, if heated under high vacuum, poly(methyl methacrylate) decomposes completely to a monomer, polystyrene forms up to 65 per cent monomer and polyethylene, only about 1 per cent.

A study of the behaviour of numerous carbon-chain saturated compounds, when heated under high vacuum, has given an insight into the influence of a number of factors on thermal stability. It has been established that the strength of the C—C bond is affected by the degree of branching of the polymer and by the presence of substituents in the macromolecule. In branched polymers the C—C bonds between the side branches and the main chain are weaker than those in the main chain. Hence, branched polymers are always thermally less stable than unbranched ones. Isotactic polymers are thermally more stable than atactic.

Substituents greatly affect the thermal stability of macromolecular compounds. The energy of the C—C bond decreases with increasing number of substituents (e.g., methyl groups) in the chain. Polyethylene is thermally more stable than polypropylene and polyisobutylene:



and polystyrene is thermally more stable than poly-α-methylstyrene:



But not all substituents lower the thermal stability of polymers. Substitution of fluorine for hydrogen atoms increases the thermal stability of a polymer. For instance, polytetrafluoroethylene is a very thermostable polymer, which does not decompose up to 400 °C. At higher temperatures it degrades to a monomer.

The presence of oxygen in the polymer (especially in the backbone chain) sharply increases the rate of thermal degradation.

The thermal stabilities of some polymers according to the data of Madorsky and Straus are given below (T is the temperature at which the polymer loses the half of its initial mass during the first 30 min of heating):

	T, °C
Poly(propylene oxide), atactic	295
Poly(propylene oxide), isotactic	312
Poly(ethylene oxide)	345
Polypropylene	387
Polyethylene	404

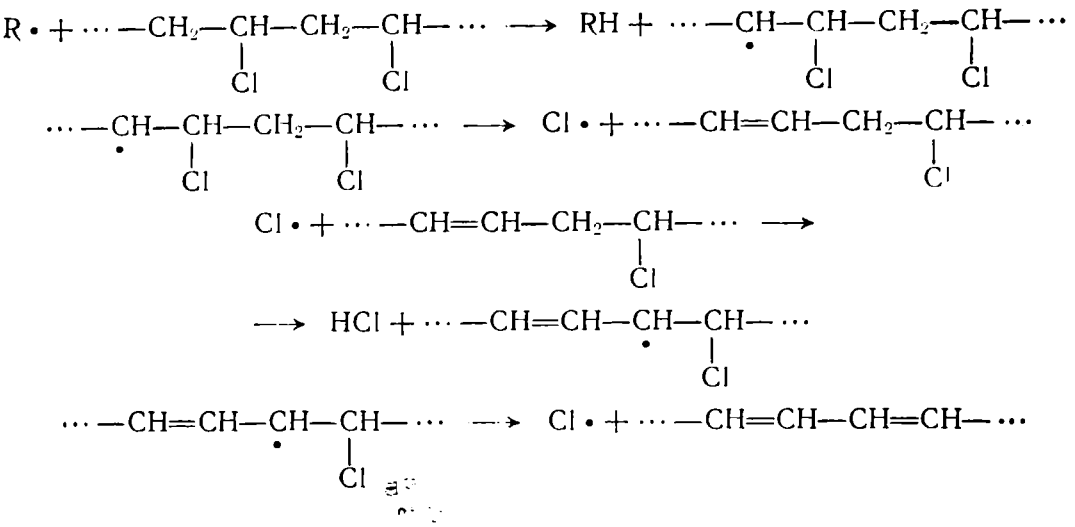
It follows from these data that polymers of ethylene oxide and propylene oxide are thermally less stable than polyethylene and polypropylene. In the general case less branched polymers are thermally more stable, especially stereoregular polymers.

Reactions Proceeding Without Rupture of the Main Chain. At an elevated temperature many polymers undergo considerable chemical and physical changes involving no bond rupture in the chain. When such polymers are heated, side substituents are eliminated, forming thermally more stable products. In some cases the products of thermal treatment lose their solubility. For example, when polymeric chlorosubstituted hydrocarbons [poly(vinyl chloride), chlorinated vinyl chloride resin *, poly(vinylidene chloride)] are heated to temperatures not over 130 °C, hydrogen chloride is eliminated and the polymer gradually loses its solubility. If these products are heated for several hours at 170 °C, almost completely insoluble products result owing to the formation of network structures. The rate of elimination of hydrogen chloride from poly(vinylidene chloride) is approximately three times as high as from poly(vinyl chloride).

The thermal decomposition of poly(vinyl chloride) evidently proceeds according to a free-radical mechanism. Decomposition reactions may be caused by traces of the initiator used during polymerization, or by radicals appearing during heating. Removal of a hydrogen atom from the methylene group of the poly(vinyl chloride) macromolecule by these radicals results in a free macroradical.

* Chlorinated vinyl chloride resin is the product of additional chlorination of poly(vinyl chloride).

The labile chlorine atom in the β-position relative to the carbon atom carrying the unpaired electron splits off as the highly mobile radical Cl·, which is capable of transferring its unpaired electron to the carbon atom of another methylene group, etc. Heating poly(vinyl chloride) gives rise to a product containing a system of conjugated double bonds:

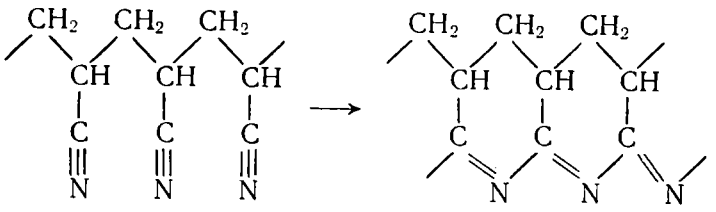


Crosslinking reactions, which may result from the recombination of two previously formed polymeric radicals, or from the interaction of a polymer radical in one chain with an unsaturated bond in another, also occur by a free-radical mechanism.

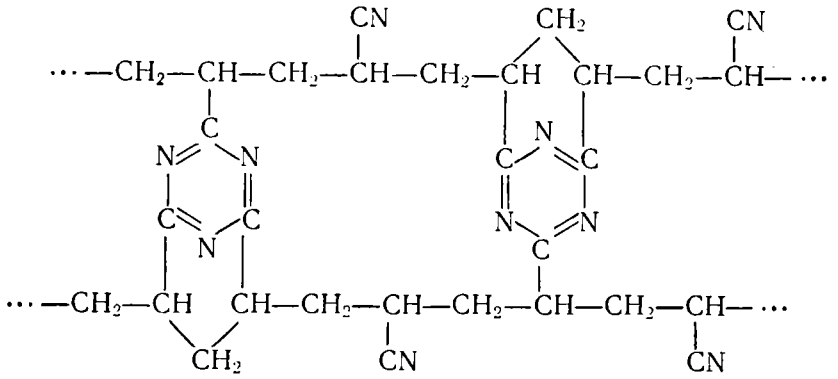
Reactions involving no rupture of the main chain may also follow an intramolecular mechanism. An example is the thermal decomposition of poly(vinyl acetate), which involves elimination of acetic acid. The C=C bond formed activates the adjacent methylene group in the poly(vinyl acetate) molecule, resulting in a system of conjugated double bonds.

Heating of nitrile derivatives involves reactions of an entirely different type. Thus, heating polyacrylonitrile in the air up to a temperature of not over 200 °C causes no noticeable changes. Further increase of the temperature brings about a gradual change in colour of a polymer (from yellow through red and brown to black), elimination of small quantities of NH_3 (up to 210 °C) and HCN (at higher temperatures) and a decrease in the solubility of the material in dimethylformamide. The infrared spectrum of the coloured samples shows that heating decreases the intensity of the absorption band corresponding to the —C≡N bond, and increases the intensity of the absorption band corresponding to the conjugated bonds —C=N—C=N—. These data suggest that at elevated temperatures the nitrile groups of polyacrylonitrile can

react with one another intramolecularly to form cycles:



or intermolecularly with the formation of network structures:



Intramolecular ring formation causes no loss of solubility in polymers. The fact that polyacrylonitrile becomes less soluble when heated can be accounted for only by the formation of three-dimensional networks.

The products of intramolecular ring formation have elevated thermal stability and semiconducting properties.

It follows from the above that the least thermostable carbon-chain polymers are polyisoprene, poly(methyl methacrylate), and polyisobutylene. Polystyrene is thermally more stable than these compounds, and polyethylene is still more stable. One of the most thermostable carbon-chain compounds is polytetrafluoroethylene. Many heterochain high polymers containing C—O bonds in their chains, e.g., cellulose and its ethers and esters (cellulose acetate, ethylcellulose, and cellulose nitrate), possess fairly low thermal stability.

The problem of producing thermally stable polymers is one of the most important problems of present-day science, and great progress has been made in this line. Among very stable organic high polymers are multiring aromatic compounds of the type of poly-*n*-phenylenes, polyarylates, and polyimides, whose thermostability may in some cases be as high as 800-900 °C.

Thermostable polymers can also be produced by the synthesis of elemento-organic and inorganic polymers, in particular, those containing Al, Ti, B, Sn, and other atoms in their main chains.

3.1.2. Mechanochemical Transformations

Mechanical degradation is a reaction of chain rupture caused by various mechanical influences the polymer is subjected to during processing (grinding, mastication, mixing, extrusion of viscous solutions or melts of polymers through capillaries, etc.) and during service of articles made of it. Thus, intensive mechanical comminution of cellulose, starch, polystyrene, polyisobutylene, and other polymers lowers their molecular mass.

Mechanical degradation of polymers, like any kind of destruction of polymers by an external mechanical influence, is caused by thermal energy fluctuations. The applied stress makes it possible for fluctuations to accumulate and confines the rupture of chemical bonds to the polymer backbone chain (Chap. 9).

Polymer degradation can be caused by a great variety of mechanical influences, e.g., high-frequency ultrasonic vibrations.

Ultrasonics is the term applied to elastic vibrations of more than 20 000 Hz frequency. Theoretically, the range of ultrasonic vibrations should extend to frequencies of 10^{13}-10^{14} Hz, above which the propagation of elastic waves is impossible, because the wavelength becomes commensurable with intermolecular distances in solids and liquids, or with the free paths of molecules in gases. At present the highest ultrasonic vibrations that have been observed have a frequency of 10^9 Hz. Ultrasonic vibrations create a field of immense intensity and very high sonic pressures. Thus, a field intensity of 10 W/cm^2 in water corresponds to a sonic pressure of the order of 6.5 atm.

The macroradicals which form are very active and can enter into various chemical reactions characteristic of macroradicals. For this reason the end products of mechanical degradation may also be different substances: compounds of lower molecular mass, and linear, branched and crosslinked polymers.

Thus, mechanical action on polymers causes chemical changes of substances, the mechanical energy being transformed into chemical energy.

Mechanochemical transformations are very important in the processing of polymers and during the service of articles made of them (related to these transformations are: fatigue of polymeric materials, the production of graft and block copolymers, etc.).

A very interesting type of mechanochemical transformation of polymers was detected by A. Berlin and coworkers. Freezing polymer solutions gives rise to such high pressures (especially in aqueous solutions), that they cause mechanical degradation of the material, which the authors call *cryolysis*. Cryolysis results in macroradicals capable, after thawing, of entering into reactions typical of free radicals.

3.1.3. Effect of Light and Ionizing Radiation

Photochemical degradation occurs under the action of light. The degree of photochemical degradation depends on the wavelength of the ultraviolet light (quantum energy), the intensity of radiation, the conditions of the experiment, and the structure of a polymer. Irradiation of some polymers with ultraviolet light (at elevated temperatures) causes depolymerization with evolution of a monomer. This process has become known as *photolysis*.

Lately great importance has been attached to the study of degradation under the action of high-energy radiations (X-rays, alpha-, beta-, and gamma-radiation). Absorption of beta- or gamma-radiation excites the polymer molecule and it dissociates either into free radicals, or into a radical and an ion. The lifetime of the ions formed is very short, and for this reason it is mainly the free radicals that enter into various chemical reactions (radiochemical transformations). The end products of degradation may be polymers of linear, branched, or crosslinked structure.

Depending on the behaviour of polymers during irradiation they fall into two groups:

1. Polymers which degrade under the action of gamma-radiation and X-rays in the solid state and in solutions of any concentration [e.g., poly(methacrylic acid), poly(vinylidene chloride)].
2. Polymers which degrade only in dilute solutions (concentrations of the order of tenths of a per cent); in the solid state and in concentrated solutions ionizing radiations cause crosslinking * in these polymers [poly(acrylic acid), poly(vinyl alcohol), polyacrylamide, poly(vinyl pyrollidone), etc.].

3.1.4. Chemical Degradation

Chemical degradation occurs under the action of various chemical agents, such as water, acids, amines, alcohols, or oxygen. The most important kinds of chemical degradation are oxidative degradation and degradation under the action of proton-containing substances.

3.1.4.1. Oxidative Degradation

Oxidative degradation of polymers is degradation by atmospheric oxygen and other oxidants.

The resistance of a polymer to oxidizing agents depends on its structure and primarily on the presence of readily oxidizable groups and bonds in its macromolecule. Oxidizable carbon-chain

* For more details on crosslinking reactions see page 78.

macromolecular compounds are unsaturated hydrocarbons, e.g., natural and butadiene rubbers.

Light and heating intensify oxidative degradation.

It has been established that double bonds in main chains are more active during oxidation than double bonds in side-chain vinyl groups. For this reason mainly linear polyenes are subject to oxidative degradation. Branched polyenes obtained as a result of 1,2-addition of dienes do not degrade upon oxidation, but form three-dimensional structures.

Ozone is a vigorous oxidizing agent. In the light, ozone degrades natural rubber strongly and this should be borne in mind when using articles made of natural rubber.

Carbon-chain saturated polymer compounds (polyethylene, polyisobutylene, and polystyrene) are more resistant to oxidation. Thus, at room temperature these polymers are practically not oxidized by atmospheric oxygen. They may degrade only if heated.

The introduction of chlorine and fluorine as substituents into polymers increases their resistance to oxidation. The most stable to the action of oxidants is polytetrafluoroethylene.

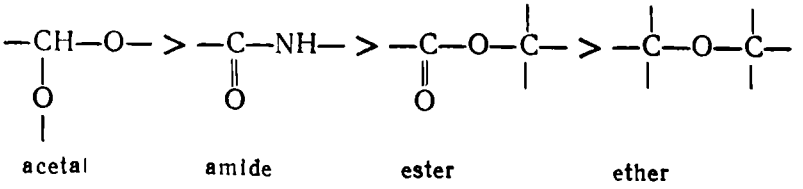
Heterochain compounds are also degraded by oxidants. The most liable to oxidative degradation are compounds containing acetal bonds, such as cellulose, which is degraded even by atmospheric oxygen.

3.1.4.2. Degradation by Chemical Agents

Chemical degradation is caused by such substances as water, acids, amines, alcohols.

Hydrolysis. This is degradation by water and aqueous solutions of acids, alkalis and salts, involving the addition of water molecules at the site of bond rupture.

Among heterochain polymers the most sensitive to hydrolysis are those which contain acetal, amide, and ether or ester linkages. In order of increasing liability to hydrolysis these bonds are arranged as follows:



Hence, the easiest to hydrolyze are cellulose and its derivatives (acetal bond) and proteins (amide bond).

Of great importance, apart from the nature of the polymer heterobond, is the hydrolyzing agent. Thus, cellulose (in the absence of oxygen) is practically not hydrolyzed by alkali, whereas dilute

acids are fairly aggressive towards the acetal bond. The strongest hydrolyzing agents are sulphuric, hydrochloric, and hydrofluoric acids, which saponify cellulose to glucose.

In the commercial preparation of cellulose acetate by the reaction of cellulose with a mixture of acetic anhydride and sulphuric acid acetylation and hydrolysis occur simultaneously. Prolonged action of this mixture on cellulose results in cellobiose octaacetate and even glucose pentaacetate.

The amide bond is second only to the acetal bond in sensitivity to hydrolysis. Heating polyamides in concentrated solutions of sulphuric, hydrochloric, or formic acids causes hydrolysis of the amide bond to form amino and carboxyl groups:

$$-NH-\overset{H}{\underset{}{\overset{|}{C}}}-\overset{OH}{\underset{}{\overset{|}{C}}}-CO- \longrightarrow -NH_2 + HOOC-$$

Elemento-organic and inorganic polymers are also subject to hydrolysis. It has been established that the most resistant to concentrated hydrochloric acid (10-30 per cent) is the linkage

$$-Ti-O-Si-$$

followed by

$$-Al-O-Si-$$

the least stable being

$$-Sn-O-Si-$$

Other conditions being equal, the —Al—O—Si— linkage in polyaluminosiloxane is more difficult to split than the same bond in kaolin (aluminosilicate).

Acidolysis and Aminolysis. *Acidolysis* is degradation under the action of carboxylic acids, involving the formation of lower-molecular products, e.g.,

$$\cdots -NH-(CH_2)_n-NH-\overset{|}{C}O-(CH_2)_m-CO-\cdots \xrightarrow{HOOC-(CH_2)_4-COOH}$$

$$\longrightarrow \cdots -NH-(CH_2)_n-NHCO-(CH_2)_4-COOH + HOOC-(CH_2)_m-CO-\cdots$$

It has been shown that the degree of degradation of substances subjected to acidolysis is proportional to the amount of the dicarboxylic acid taken for the reaction. The longest chains are especially liable to acidolysis. This process results in products of close molecular masses.

Aminolysis is brought about by the action of amines. An example is the reaction that occurs when polyamides are heated with hexamethylene diamine:

$$\cdots -NH-(CH_2)_n-NH-\overset{|}{C}O-(CH_2)_m-CO-\cdots \xrightarrow{NH_2-(CH_2)_6-NH_2}$$

$$\longrightarrow \cdots -NH-(CH_2)_n-NH_2 + NH_2-(CH_2)_6-NH-CO-(CH_2)_m-CO-\cdots$$

In this reaction the degree of degradation of polymer is proportional to the amount of diamine taken for the reaction.

3.2. CROSSLINKING REACTIONS

Crosslinking (or *structurizing*) are reactions of formation of chemical crosslinks between macromolecules, resulting in polymers with network structures. These reactions may occur during polymer synthesis as well as during processing of linear polymers. During polymer synthesis crosslinking of chains is in most cases undesirable, because it results in insoluble and nonmelting products which are difficult to remove from the reactor. Therefore, products of polymerization and polycondensation are usually polymers of linear or branched structure. In fabricating articles from such polymers crosslinking reactions are often carried out purposely. These reactions are commonly known as *vulcanization* in the rubber industry and *curing* or *hardening* in the plastics industry. They may be caused by heating or by the action of ionizing radiations.

Crosslinking of polymers under the action of ionizing radiations is known as *radiation crosslinking*. This process has been studied the most thoroughly for polyethylene, the irradiation of which leads to elimination of hydrogen and increases the degree of unsaturation of the molecules. The mechanism of the process reduces to the following. Under the action of gamma-rays the polyethylene molecule generates free radicals, which react with a molecule or with another macroradical, each forming a branch or bridge (crosslink). Abstraction of a hydrogen atom from the methylene group results in the formation of double bonds and crosslinks.

The number of crosslinks formed can be estimated from the amount of hydrogen liberated.

Radiation crosslinking of polyethylene and other polymers gives materials of increased thermal stability, insoluble in organic solvents and possessing a number of other valuable properties. It is a process of great practical importance.

Radiochemical transformations are also used for preparing block and graft copolymers.

If the number of crosslinks is small (low network density), the product will be soft and flexible; increasing the network density increases the stiffness of the polymeric material. A very large number of crosslinks gives a very hard material.

Chemical crosslinks in polymers may form directly between the carbon atoms of adjacent macromolecules without the participation of other substances, or with the aid of various compounds added specially to the system. Such substances are called *vulcanizing* or *hardening agents*

Polymers that form three-dimensional networks are commonly known as *thermohardening polymers*, or *thermosets.*

Polymers in which no chemical crosslinks form on heating and which become soft at a certain temperature, passing from the solid to a plastic state, are called *thermomelting* or *thermoplastic polymers.*

Sometimes the polymer itself is not thermosetting, but becomes a thermoset when mixed with a vulcanizing (curing) agent. In thermosetting polymers (or mixes) crosslinks may form even at room temperature, but only at a very low rate. This is important for the storage of thermosetting mixes.

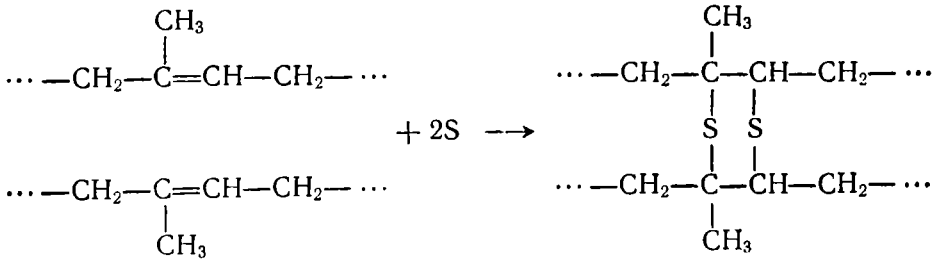
With rising temperature the rate of most known crosslinking reactions increases sharply. Therefore, in practice vulcanization and curing reactions are usually carried out with heating. At present polymer-vulcanizing agent systems are known which cure rapidly even in the cold (cold vulcanization, cold curing).

The technically most important crosslinking reactions are discussed below.

3.2.1. Vulcanization of Rubbers

Many natural and synthetic rubbers are not themselves thermosetting materials. To form three-dimensional networks in them they are reacted with special vulcanizing agents (usually sulphur).

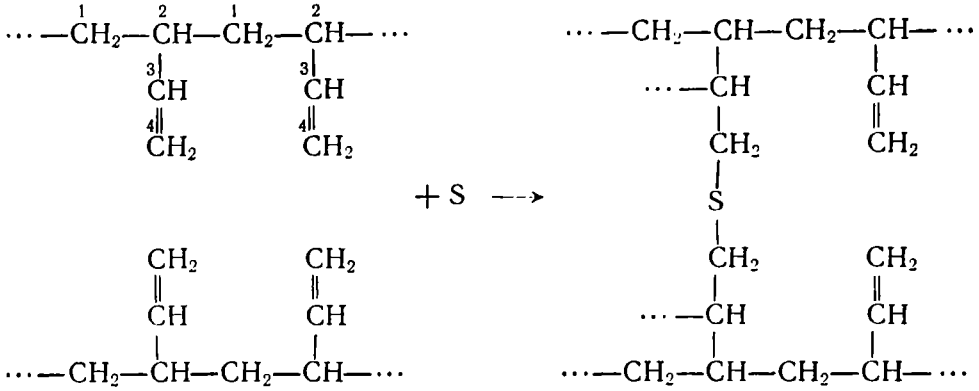
When sulphur reacts with two rubber macromolecules, it adds on at the point of opening of double bonds to form a so-called sulphur bridge:



Other vulcanizing agents are selenium, tellurium, and oxygen. In practice natural and synthetic isoprene, butadiene, styrenebutadiene, nitrile and butyl rubbers are vulcanized with sulphur. At low sulphur content (2-3 per cent by weight) the rubber is soft and flexible; a sulphur content of 32 per cent by weight gives a hard product called ebonite.

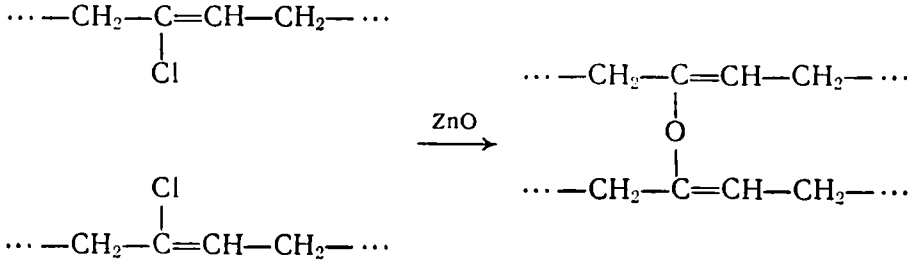
Vulcanization of polybutadiene differs from that of natural rubber. If the units in the polybutadiene molecules are joined in the 1,2-position, the sulphur interacts at the point of opening of the

double bonds of the vinyl side groups, e.g.,



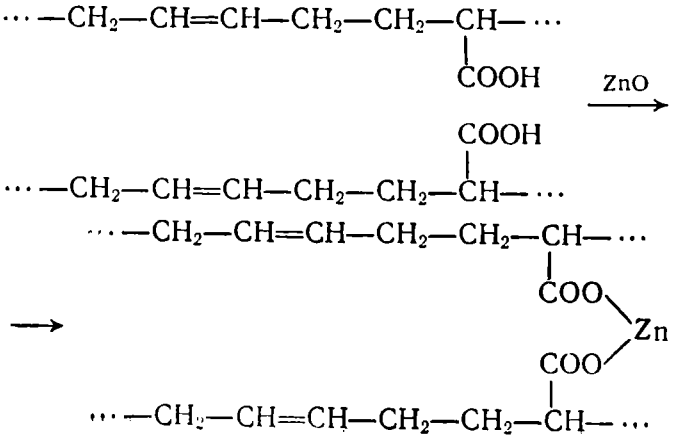
When butadiene rubber macromolecules react with atmospheric oxygen, the crosslinking reactions form oxygen bridges between the vinyl groups. It has been shown that rubbers can be crosslinked even in the absence of oxygen (under vacuum) if heated. This forms the basis for the preparation of thermoebonite and a butadiene rubber of network structure (Escapon).

Crosslinking reactions may also occur without opening of double bonds (substitution reactions). An example of such a reaction is the vulcanization of polychloroprene by metallic oxides:



Vulcanization of polychloroprene involves no change in unsaturation.

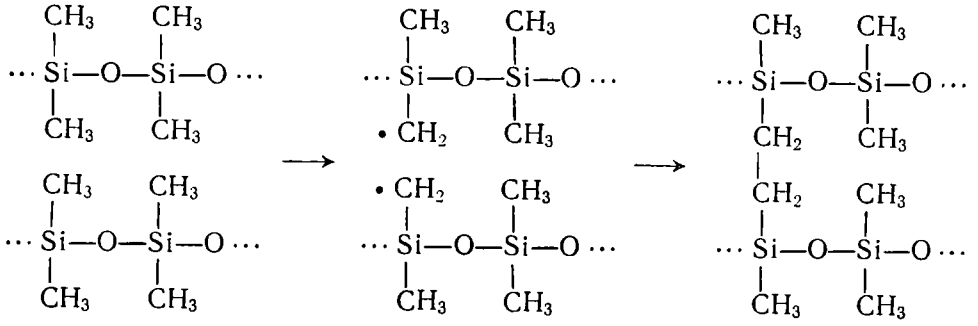
The reaction of vulcanization of carboxylate rubbers by polyvalent metallic oxides is given below by way of example:



Of special interest is the vulcanization of silicone rubbers. These rubbers are saturated compounds and therefore cannot be vulcanized by sulphur. Three methods of crosslinking them are known.

According to the first method, which is the most popular in industry, vulcanization of silicone rubbers is carried out in the presence of benzoyl peroxide, which decomposes readily on heating into free radicals.

The reaction proceeds by a radical mechanism:



According to the second method silicone rubbers are vulcanized by radiation crosslinking.

The third method consists in vulcanizing the silicone rubbers in the cold by tetraethoxylenes and stannumorganic compounds of the general formula

$$R_2Sn(OAc)_2$$

where R = ethyl or butyl radical
Ac = acetyl, capryl, or stearyl.

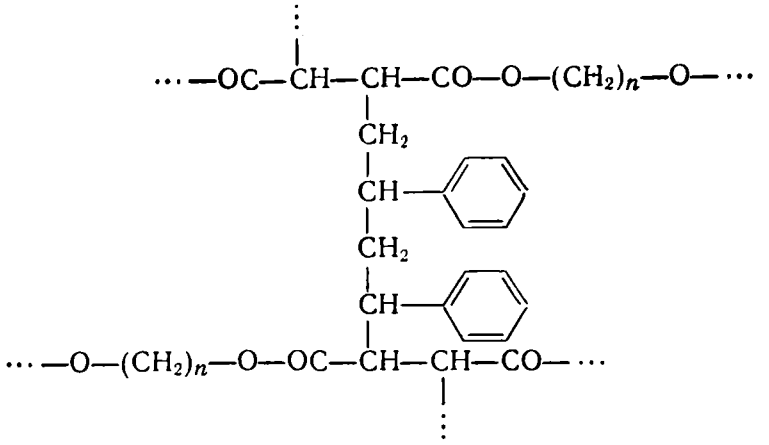
3.2.2. Hardening of Plastics

In the plastics industry hard articles (i.e., articles of high network density) are produced by curing mainly polycondensation products of linear structure and low molecular mass. At elevated temperatures these products are liquids, which transform on cooling into brittle solids. The resulting material is ground to what is known as a moulding powder and charged into the mould. When this powder is heated, crosslinking occurs forming a hard nonmelting and insoluble product. For example, when phenol-formaldehyde polymers are heated, they pass readily from the resol form to resitols, the latter being elastic products of low network density, which change on further heating into resites, hard products of high network density.

One of the curing agents used for phenol-formaldehyde resins is hexamethylene tetramine (urotropin).

Curing by polymerization has lately become fairly common practice. For instance, the monomer can be polymerized in the pre-

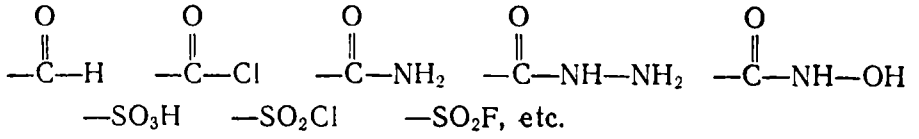
sence of low-molecular unsaturated polyesters. The growing macroradicals interact with the double bonds of the polyester, forming a polymer of network structure:



3.3. REACTIONS OF FUNCTIONAL GROUPS

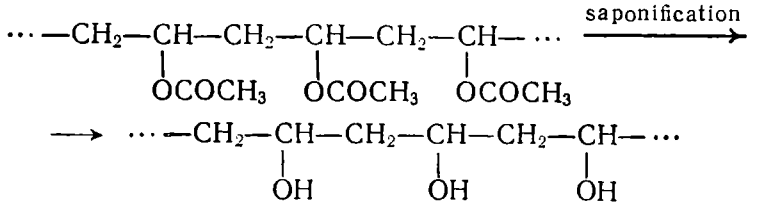
Many polymers cannot be obtained by direct polymerization or polycondensation from low-molecular compounds either because the initial monomers are unknown, or because they will not polymerize. It is therefore necessary at times to synthesize polymers from other macromolecular compounds containing reactive groups. In carrying out such syntheses the reaction conditions must be selected so as to prevent the possibility of degradation of molecular chains. Then, as a result of chemical transformations the chemical composition of a polymer will change with no substantial decrease in degree of polymerization. Staudinger called such reactions *polymer-analogous transformations.*

Polymer-analogous transformations are possible for compounds with a great variety of functional groups, e.g.,



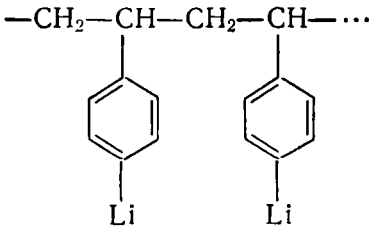
The commercial methods of preparing many polymers are based on reactions of this kind. Various cellulose esters (acetate, nitrate, etc.) are obtained in industry by esterification of cellulose. The hydroxyl groups of cellulose are replaced by $-OCOCH_3$ and $-ONO_2$. In addition to the known ethers and esters of cellulose, phenyl ethers $[C_6H_7O_2(OH)_2OC_6H_5]_n$, and esters with amino acids $[C_6H_7O_2(OH)_2OCOC_6H_4NH_2]_n$, phosphorus-containing acids, etc., have been prepared lately.

Poly(vinyl alcohol) is also obtained from a polymer already made by the acid or alkaline saponification of poly(vinyl acetate):



Poly(allyl alcohol) is obtained by reducing polyacrolein, from which polymeric oximes, hydrazone, phenylhydrazone, and other analogues of corresponding low-molecular organic substances can also be prepared.

A very interesting reaction is that of the production of macromolecular compounds containing alkali and alkali-earth metals, e.g., the synthesis of poly-*p*-lithiumstyrene. Isotactic crystalline polystyrene is first converted into poly-*p*-iodostyrene, which is subsequently reacted with butyllithium to form poly-*p*-lithiumstyrene:



Thus, polymer-analogous transformations make it possible to create new classes of polymers and to vary the properties and fields of application of the finished products over a wide range.

3.4. INTRAMOLECULAR REARRANGEMENTS

These reactions have already been discussed in Chap. 2 and partly in this chapter. They include reactions of dehydrochlorination of poly(vinyl chloride) to polyvinylenes, reactions of intramolecular cyclization of polyacrylonitrile and some others, involving rearrangements within the polymer chain.

3.5. STABILIZATION OF POLYMERS

The questions dealt with in this chapter are of great importance for the processing of polymers and for the usage of finished polymeric articles. Processing is not only imparting a definite shape to the material; it is the creation of a quality which depends to a considerable extent on the chemical processes caused by mechanical action, heat, atmospheric oxygen, light, etc. These agen-

cies bring about degradation, oxidation, and crosslinking. The free radicals that form enter into secondary reactions, giving branches and crosslinks.

The thermooxidative and mechanochemical transformations that occur inevitably during processing in the long run sharply deteriorate the quality of the polymeric material. The processing of polymers always involves partial destruction, and the task of the technologist dealing with processing of polymers consists in slowing down as far as possible the chemical reactions that result in destruction of polymers.

This can be done in two ways: by using very pure monomers, and by adding special substances called *stabilizers*.

As a rule, compounds used as stabilizers are modifiers of the chain reactions of polymer decomposition, i.e., free-radical acceptors.

Despite the great variety of phenomena involved in the destruction of polymers, the most important among them are the chain processes of oxidation and decomposition of macromolecules. As was shown above, all mechanochemical and thermooxidative transformations proceed by a chain reaction mechanism. For this reason, all kinds of impurities in the polymer, capable of readily breaking down into free radicals or ions, may act as initiators of these processes.

Hence, polymers synthesized from insufficiently pure monomers, or which have not been purified sufficiently thoroughly themselves, are always difficult to process. But even in very pure polymers, at sufficiently high temperatures all the processes enumerated do occur. The temperature region of polymer processing is the region between the melting point and the point of thermal decomposition. This region should be as wide as possible. Widening it by lowering the melting point or glass-transition temperature (see p. 211) of polymer is not advisable, since this lowers the thermal stability (see Chap. 8) of the material and its service qualities. Therefore, the temperature region of processing should be widened by raising the decomposition temperature of a polymer, i.e., by adding stabilizers.

Nowadays most polymers are processed with incorporation of stabilizers which prevent aging, i.e., changes in properties with time, under the conditions of service of the polymeric articles.

Stabilization in the broad sense of the word consists in preserving the initial properties of polymers under various influences. Owing to the variety of chemical processes occurring during the destruction of polymers stabilization of all polymers cannot be effected by a single procedure. Each polymer requires its specific stabilizers. But since all decomposition reactions are chain reactions they can all be retarded by three methods:

(1) by suppressing the chain reactions developing in the course of thermal and thermooxidative decomposition;

(2) by setting up conditions under which the substances formed during decomposition prevent further decomposition of the polymer;

(3) by setting up conditions under which the decomposition will occur reversibly.

The most commonly used in practice is the first method.

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CHAPTER 4

Polymer Chain Flexibility

The physical properties of polymers depend on their chemical constitution. However, the interrelation between physical properties and chemical constitution of polymers is very complex. To understand this relation we must first get an insight into the concept of *polymer chain flexibility.*

Until 1934 macromolecules were regarded as very long stiff rods. However, a number of very important properties of polymeric materials could not be accounted for on the basis of this concept. That is why, for instance, to explain the ability of natural rubber to undergo very large recoverable deformations, it was suggested hypothetically that its macromolecules have helical form, uncoiling when a load was applied and coiling up again when the load was removed.

This notion lacked scientific grounding.

The present-day concept of the shape of macromolecules arose in connection with the discovery of a specific type of thermal motion, namely, internal rotation of separate parts of the molecule relative to one another.

4.1. INTERNAL ROTATION IN MOLECULES. ROTATION BARRIER

Let us consider the phenomenon of internal rotation for the simple organic compound ethane and its derivatives.

In the ethane molecule the carbon atoms are joined to the hydrogen atoms through covalent bonds (σ bonds). This accounts for the tetrahedral arrangement of substituents with an angle of 109° 28′ between the directions of the σ bonds (valence angle).

Figure 4.1 is a schematic representation of the ethane molecule.

Van't Hoff suggested that both CH_3 groups possess unrestricted free rotation about the direction of the chemical bond connecting them. Such rotation of one part of a molecule relative to another is now called *internal rotation* in the molecule.

Free rotation is rotation which causes no change in energy of the molecule. In the ethane molecule all the hydrogen atoms are equivalent, and it may therefore be assumed that whatever its arrangement in space, the potential energy of the molecule should be the same, i.e., that rotation is free. However, internal rotation in the ethane molecule is not actually free owing to the interaction between chemically unlinked neighbouring atoms.

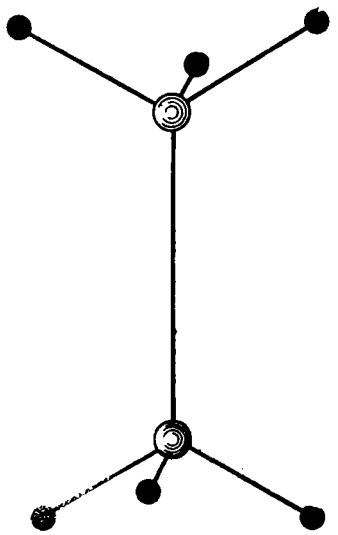


Fig. 4.1. Model of ethane molecule

Owing to thermal motion the spatial arrangement of the atoms keeps changing continuously. To each position of the atoms corresponds a definite value of potential energy of the molecule, which is determined by all the interactions between atoms, electrons, nuclei, etc.

When the CH_3 group of the ethane molecule rotates about the line connecting the carbon atoms, the potential energy U changes, i.e., $U = f(\varphi)$, where φ is the angle of rotation.

Suppose that the atoms in the ethane molecule are arranged as shown in Fig. 4.2*a*, and the potential energy of the molecule is U_1. To assume a new position differing maximally from this, one of the CH_3 groups must rotate relative to the other through 60° (Fig. 4.2*b*). The potential energy corresponding to this new arrangement equals U_2. If the CH_3 group rotates through another 60°, the molecule will repeat the arrangement shown in Fig. 4.2*a*.

It becomes evident now that $U_1 \neq U_2$, i.e., the different positions of one methyl group relative to the other are energetically not equivalent. The least advantageous position is that where the hydrogen atoms of the two methyl groups are situated exactly beneath each other, as shown in Fig. 4.2*b*, because in this case forces of repulsion arise between them, tending to return the atoms to their energetically most advantageous, stable position, the one shown in Fig. 4.2*a*. Assuming the potential energy of the molecule with the atomic arrangement illustrated by Fig. 4.2*a* to be zero, the potential energy corresponding to the model shown in Fig. 4.2*b* will be maximum.

The dependence of the potential energy of the ethane molecule on the angle of rotation φ of its methyl group is shown in Fig. 4.3. The U vs. φ curve for molecules of lower symmetry (as compared to the ethane molecule) such as *n*-butane or dichloroethane has

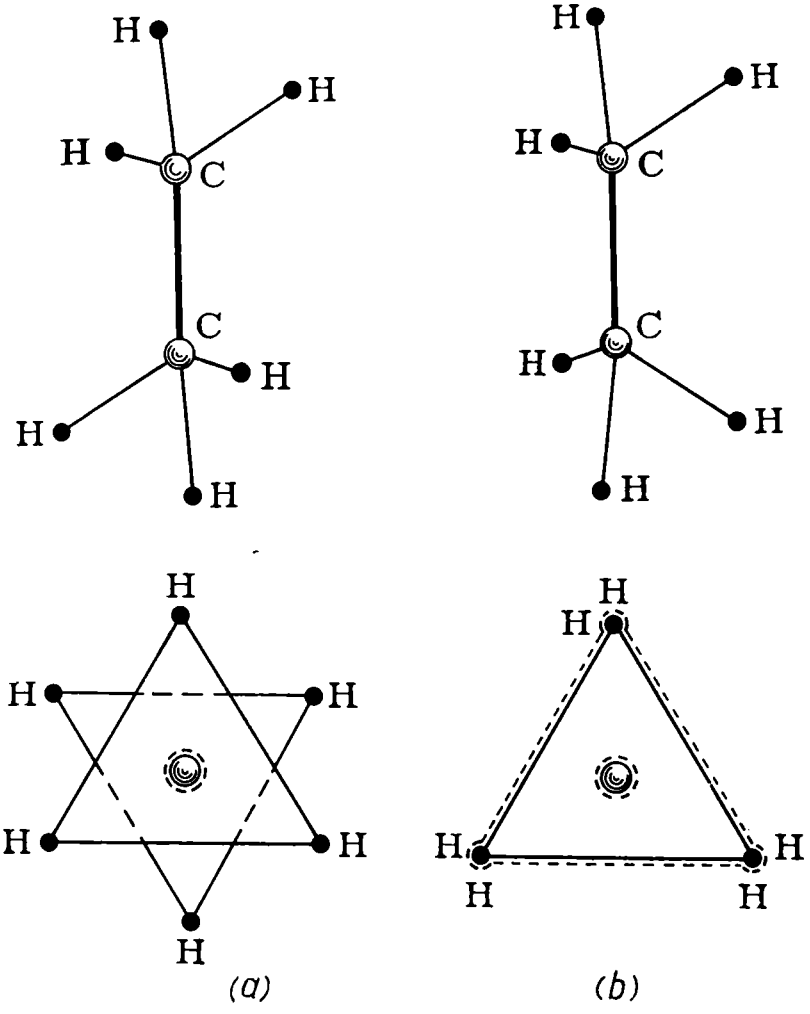


Fig. 4.2. Various spatial arrangements of hydrogen atoms in ethane molecule (below: projections of molecule):
a — *trans*-arrangement; *b* — *cis*-arrangement

a more complex shape (Fig. 4.4). This curve has three minima corresponding to the angles φ=0, 120, and 240°, but the depths of the minima are not equal. Figure 4.5 shows the molecular shapes corresponding to these energy minima. The deepest minimum corresponds to the planar, so-called *trans* form possessing a centre of symmetry. The other two minima correspond to the out-of-plane or *gauche* forms. These result from the *trans* form if the methyl group is rotated through 120°, and are mirror images of each other.

The energies of the two *gauche* forms are equal and exceed the energy of the *trans* form by about 500-800 cal/mole.

The energy required for the molecule to move from the position with minimum potential energy to that corresponding to its maximum value is called the *hindrance potential* or *potential rotation barrier.*

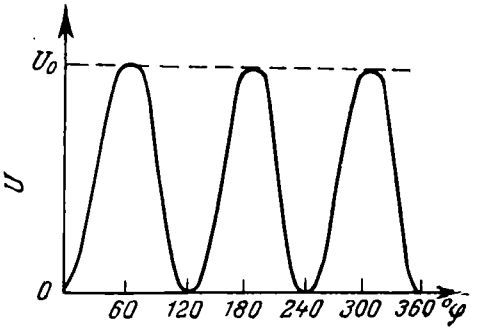


Fig. 4.3. Dependence of potential energy of ethane molecule on angle of rotation of methyl group

The presence of energy barriers makes rotation of the groups in the ethane or 1,2-dichloroethane molecules nonuniform. Under ordinary conditions the molecule tends to pass from the energetically least advantageous to the most advantageous position. Rotation from the most advantageous position (potential well) to the least advantageous one (hump) is possible only if the kinetic energy of the molecule exceeds the height of the potential energy barrier.

If the supply of kinetic energy is small, the groups of the molecules cannot depart from the positions corresponding to the minimum potential energy (they are as if held fast in these positions). In this case no rotation occurs and the molecular groups only vibrate about the minimum energy positions. This phenomenon has become known as *restricted* or *retarded* internal rotation.

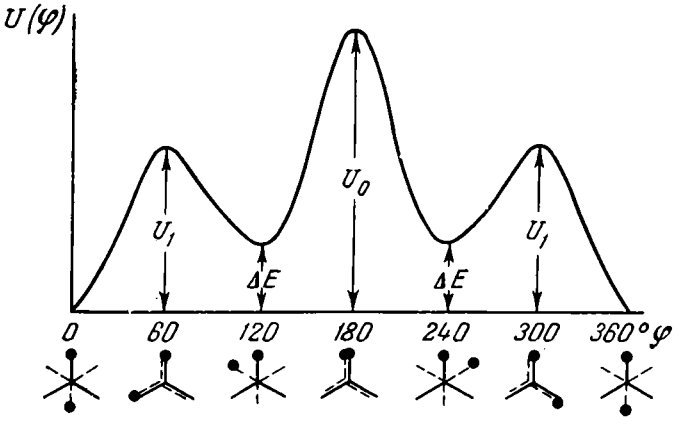


Fig. 4.4. Dependence of potential energy of the molecules of 1,2-dichloroethane and *n*-butane on the angle of rotation φ. At the bottom are shown the projections of the molecules corresponding to different arrangements of chlorine atoms (or CH_3 groups) and hydrogen in space; solid dots are chlorine atoms (or CH_3 groups)

Restricted rotation of individual groups may occur not only about the direction of an ordinary C—C bond, but also about those

of C—O, O—N, Si—O, and other bonds, the rotation barrier usually depending on interactions between atoms which are not linked to each other chemically, but are linked to the atoms forming the bond around which rotation occurs.

The heights of potential energy barrier for rotation U_0 have been calculated from the thermodynamic properties of ideal gases,

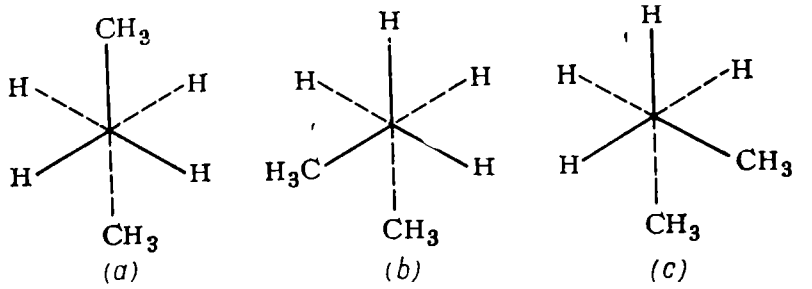


Fig. 4.5. Rotational isomers of *n*-butane (projection on plane perpendicular to central C—C bond):
a—*trans* form; *b*, *c*—*gauche* forms

i.e., for isolated molecules. The calculated values of U_0 given below show that the potential energy barriers hindering the rotation of most organic compounds range from 1 to 4.5 kcal/mole:

	U_0, kcal/mole		U_0, kcal/mole
$H_3C—CH_3$	2.8	$H_3C—CF_3$	3.70±0.45
$H_3C—C_2H_5$	3.40	$H_3C—OH$	1.07
$H_3C—CH(CH_3)_2$ . . .	3.90	$H_3C—SH$	1.06
$H_3C—C(CH_3)_3$ . . .	4.40	$H_3C—NH_2$	1.90
$H_3C—CH=CH_2$ . . .	1.95	$H_3C—SiH_3$	1.70
		$F_3C—CF_3$	4.35

The energy barrier of the ethane molecule is comparatively low, and the kinetic energy of this molecule at room temperature is sufficient to cause free rotation. That is why ethane is in fact a mixture of molecules whose atoms may occupy different positions in space. The transition from one position to another occurs approximately 10^{10} times per second, making it practically impossible to separate ethane molecules with different atomic arrangements. That these different arrangements actually exist can however be shown by spectroscopic techniques.

Potential energy barriers increase with increasing number of CH_3 groups in the molecule, and in the presence of unsymmetrically arranged chlorine or fluorine atoms. They are decreased by the presence of a double bond next to the ordinary bond around which rotation occurs (e.g., compare butane and butylene). The energy barriers for rotation around C—O, C—S, and C—Si bonds are comparatively small.

4.2. CONFIGURATION AND CONFORMATION OF MOLECULES

The molecule of any substance has a chemical constitution to which corresponds a strictly definite spatial arrangement of atoms, or a definite *configuration.*

The configuration of the ethylene molecule is shown schematically in Fig. 4.6.

The double bond is formed by two pairs of electrons belonging to the linked carbon atoms. One of these electron pairs forms an ordinary covalent σ bond, and the second pair forms what is

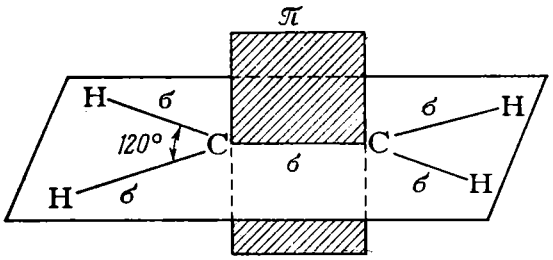
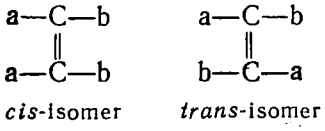


Fig. 4.6. Model of ethylene molecule

known as a π bond. The specific configuration of the electron cloud of the π bond fixes the direction of the other four covalent σ bonds of the two carbon atoms. These bonds are arranged in the same plane at an angle of 120° to each other and to the direction of the σ bond between the carbon atoms joined by the double bond (see Fig. 4.6).

Compounds with double bonds in which the carbon atoms have two different substituents (a and b) may be represented by the formulas:



It follows, therefore, that ethylene derivatives are capable of *spatial isomerism* (*stereoisomerism*), stipulated by different arrangements of substituents relative to the double bond. This type of spatial isomerism is known as *cis-trans* isomerism. A classical example of such stereoisomers are fumaric and maleic acids.

In contrast to compounds with double bonds, saturated compounds in most cases do not display *cis-trans* isomerism, even if they have different substituents at the same carbon atom. The absence of stereoisomers is due to very rapid internal rotation of the groups relative to each other. However, if the potential energy barriers are sufficiently high, molecules of definite three-dimensional

structures can be singled out even in the case of saturated compounds.

Rotation of separate groups may also occur around a double bond but for this it is necessary to break the π bond, which naturally requires a large amount of energy. For this reason internal rotation does not occur at ordinary temperatures. But at sufficiently high temperatures, when the energy of thermal motion becomes commensurable with the energy of chemical bonding, mutual transformations of *cis-* and *trans*-isomers become possible.

Thus, rotation of one part of the molecule relative to another may or may not involve rupture of chemical bonds. In the former case the molecule is said to have different *configurations* before and after rotation.

A change in molecular shape caused by thermal motion or by the action of an external field, involving no rupture of chemical bonds, is called a *conformational change.* Molecular shapes which pass into one another without rupture of chemical bonds are called *conformations* or *rotational isomers.*

4.3. INTERNAL ROTATION IN MACROMOLECULES

The idea of internal rotation of polymer molecules is due to Kuhn, Mark, and Guth, who suggested that chain units could rotate freely relative to each other.

Consider a single isolated polymer chain whose carbon atoms are linked only by σ bonds. The units of this chain are in thermal movement, i.e., one unit can rotate relative to its neighbour. Suppose the valence angles of the chain are not fixed and the units rotate freely about the σ bonds. This is known as the *freely jointed chain model.* Obviously, the units of a freely jointed chain can assume arbitrary orientation independent of that of their contiguous units. Such a chain can assume any conformations, and is *perfectly flexible* (Fig. 4.7).

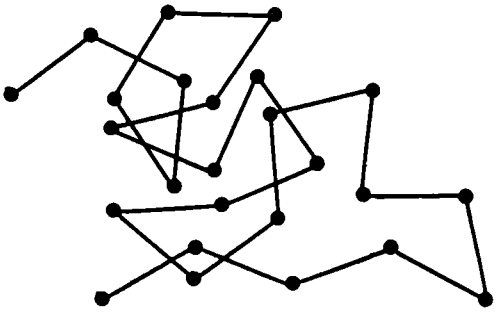


Fig. 4.7. Conformations of a freely jointed chain

The valence angles of real polymer chain molecules have a definite value (Fig. 4.8), which during rotation of their units can change only insignificantly. In a chain with fixed valence angles the position of each subsequent unit is dependent on that of the preceding one (Fig. 4.9). Therefore, even with free rotation, such a chain will assume a smaller number of conformations than a freely jointed chain, but still it can also bend greatly.

Bresler and Frenkel showed that internal rotation in polymer molecules is retarded by interactions between atoms not bonded chemically to each other. These may be interactions between atoms

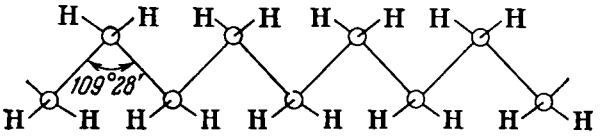


Fig. 4.8. Model of a hydrocarbon chain

of the same chain (intramolecular interaction) or between atoms belonging to units of neighbouring chains (intermolecular interaction).

Intermolecular interaction is one that takes place between molecules not reacting chemically with each other. *Intramolecular interaction* is nonchemical interaction between the units of a molecule. It is customary to divide these two kinds of interaction into ionic, orientational, deformational, and dispersional interactions. Besides, hydrogen bonds may arise between adjacent molecules and even between certain groups of the same molecule.

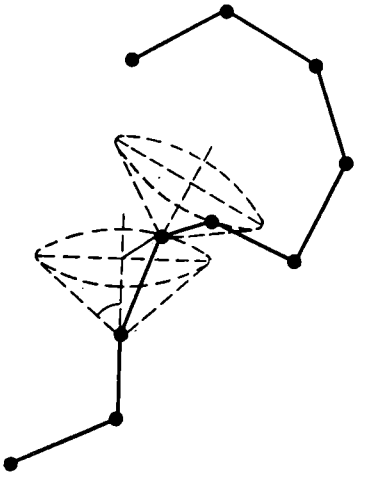


Fig. 4.9. Conformations of a chain with fixed valence angles

Ionic interaction is electrostatic attraction or repulsion between charged particles. The energy of ionic interaction decreases in inverse proportion to the square of the distance between the ions. Such an interaction can occur at fairly large distances (longrange forces).

Orientational interaction is an interaction between uncharged molecules of dipole structure. Its energy is given by the equation *:

$$U_{or} = -\frac{2}{3} \cdot \frac{\mu_1^2 \mu_2^2}{kTr^6} \tag{4.1}$$

where μ_1 and μ_2 = dipole moments of the two molecules
T = absolute temperature
k = Boltzmann constant
r = separation of molecules.

* Here and in the following the minus sign on the right-hand side of the equation denotes attraction.

Deformational interaction is one between a polar molecule and a nonpolar one which is polarized in the field of the dipole. The polarization consists in a shift of electrons in the nonpolar molecule to form a so-called *induced dipole.* The energy of this interaction is determined by the equation

$$U_{def} = -\frac{2}{r^6}\mu^2\alpha \tag{4.2}$$

where μ = constant dipole moment of polar molecule
α = polarizability of nonpolar molecule
r = distance between them.

All the types of interaction discussed above are electrostatic interactions. However, in contrast to ionic, orientational and deformational interactions occur only over very small distances, because their energy decreases in inverse proportion to the sixth power of the distance between the molecules (short-range forces).

Dispersional interaction can occur between any molecules, whether polar or nonpolar. The origin of dispersion forces is explained by the laws of quantum mechanics, according to which the energy of this type of interaction is given by the equation:

$$U_{disp} = -\frac{3}{2}\cdot\frac{1}{r^6}\cdot\frac{I_1 I_2}{I_1 + I_2}\alpha_1\alpha_2 \tag{4.3}$$

where α_1 and α_2 = polarizabilities of the two interacting molecules
I_1 and I_2 = ionization potentials of the molecules
r = separation of the molecules.

Dispersion forces are also short-range forces, effective over a distance of 3-4 Å.

It follows from the above equations that the only kind of interaction that depends on temperature is orientational interaction. With rising temperature thermal motion disturbs the orientation of the dipoles, and the absolute value of the energy decreases [Eq. (4.1)]; at an infinitely high temperature U becomes zero.

Dispersional interaction occurs between any molecules, but in the case of polar molecules it is superimposed by orientational interaction. Hence, the total energy of interaction between polar molecules or polar groups is higher than between nonpolar ones. Thus, if the energy of interaction between $-CH_2-$ or $-\underset{|}{CH}-\underset{|}{CH}-$ hydrocarbon groups is about 1.0 kcal/mole, the interaction energy between $-\underset{|}{\overset{|}{C}}-Cl$ groups is around 3.4 kcal/mole.

A special type of interaction, intermediate between chemical and nonchemical, is the interaction between atoms resulting in the

formation of a *hydrogen bond*. The hydrogen atom is much smaller in volume than other atoms, and therefore can approach atoms joined by a covalent bond very closely. If the hydrogen atom is linked chemically to an electronegative atom, then, when the two molecules come close enough to make proton transfer possible, the proton is attracted to both atoms of the approaching molecules (Fig. 4.10). Such a linkage between two atoms of different molecules "via hydrogen" is called the hydrogen bond. The energy of the hydrogen bond is higher than that of orientational or dispersional interaction. The hydrogen bond can be formed by —OH,

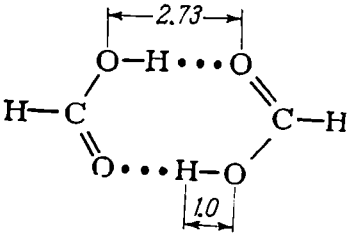


Fig. 4.10. Formation of a hydrogen bond

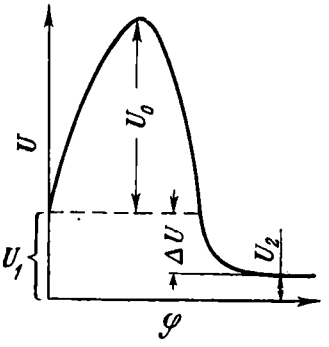


Fig. 4.11. Activation energy of rotation of a hydrocarbon chain depending on angle of rotation of its unit

—COOH, —NHCO— and other groups. The presence of hydrogen bonds between molecules is responsible for the association of molecules in the liquid and vapour states, for increased viscosity of liquids, and for changes in a number of other properties of substances.

There are cases where stable intramolecular hydrogen bonds exist between atoms of the same molecule.

In real systems polymer molecules are surrounded by other similar molecules and, hence, there is always some kind of intermolecular interaction between them, which affects the degree to which rotation is retarded. However, it is very difficult to take this interaction into account. Therefore, in quantitative calculations one takes account only of intramolecular interaction between chemically unlinked atoms and groups of atoms. Two kinds of intramolecular interaction are distinguished:

1. *Short-range interaction*, i.e., interaction between atoms or groups of atoms with small distances between them, e.g., between the atoms of adjacent units.

2. *Long-range interaction*, i.e., interaction between atoms or atomic groupings of units situated at considerable distances from one another in the chain. This kind of interaction is displayed

when a long chain coils up. Then units separated by considerable length of chain may come close to each other by chance, and attraction or repulsion will arise between them.

Free rotation is retarded due to short-range interaction.

The potential energy of a polymer molecule changes when one part of the molecule rotates relative to another owing to intramolecular interaction. A U vs. φ dependence similar to those shown above (see Figs. 4.3 and 4.4) can be plotted for each chain molecule. The shape of the curve depends on the chemical constitution of the polymer. Usually this curve has a complex shape with several minima.

If one position of a chain unit is characterized by the potential energy U_1, and another, which the unit acquires as the result of thermal motion, by the energy U_2, the energy of transition from one position into the other is equal to the difference of these energies: $\Delta U = U_2 - U_1$ (Fig. 4.11). The energy difference ΔU determines the flexibility of polymer chain realized at thermodynamic equilibrium, known as its *thermodynamic flexibility.*

The thermodynamic flexibility of a chain gives an idea of the ability of the chain to undergo conformational transformations. But another essential factor in addition to the ability to bend is the rate of transition from one position into another. The rates of conformational transformations depend on the ratio of the potential energy barrier U_0 and the energy of external influences (thermal motion and mechanical or other force fields). The higher the value of U_0, the slower will the units rotate, and the smaller will be the flexibility of the polymer chain. Chain flexibility determined by the value of U_0 is known as the *kinetic flexibility.* Thermodynamic and kinetic flexibilities do not necessarily coincide: in a chain of high thermodynamic flexibility the rate of rotation of the units may be not very high, i.e., the chain may behave like a rigid chain.

Rotation of units and their passage from an arrangement corresponding to one energy minimum to one corresponding to another energy minimum can occur only if there is an ample supply of energy. Even so, the links cannot assume just any position in space, but only those allowed by the presence of an interaction. Thus, owing to intramolecular interactions, a real polymer chain assumes a smaller number of conformations than a freely jointed chain.

However, if the macromolecule does not possess the necessary supply of energy, its units will not rotate but will engage in a peculiar kind of thermal movement consisting in *torsional vibrations* about the position of minimum energy. These vibrations also add flexibility to the macromolecular chain; the more intensive they are, the more flexible will the molecule be.

Polymers with sufficiently intensive torsional vibrations are known as *flexible-chain polymers*. Polymers with hindered rotation of one part of a chain relative to another one are known as *rigid-chain polymers*. They include ladder polymers, polymers with condensed aromatic nuclei, and polyalkylisocyanates (see Chap. 1).

4.4. CONFIGURATION AND CONFORMATION OF MACROMOLECULES

A long polymer chain can assume various configurations and conformations. For example, chains composed of isoprene residues joined by 1,4-bonds may have two stable configurations: the *cis*-configuration (natural rubber) and the *trans*-configuration (gutta-percha) (see p. 41). Other stable configurations are the chains

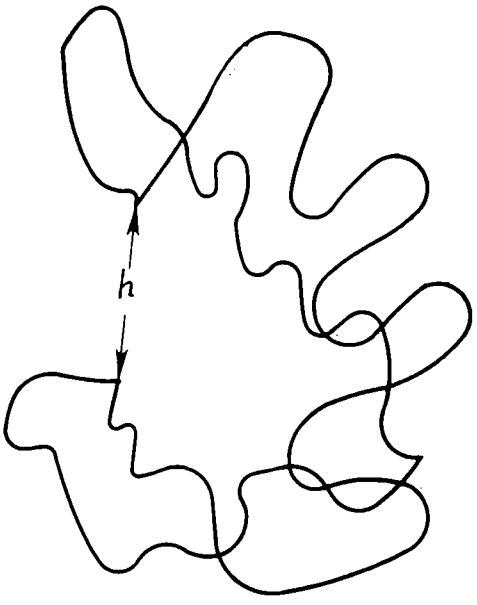


Fig. 4.12. Different conformations of a chain (*h* is end-to-end distance of chain)

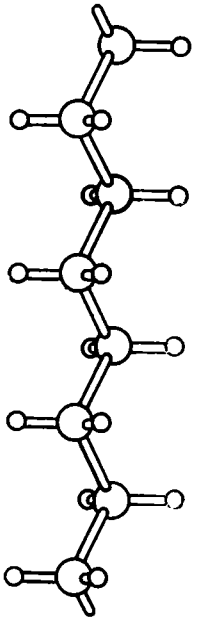


Fig. 4.13. Macroscopic model of ordered structure of polyethylene chain sections

of syndiotactic and isotactic polystyrene and of syndiotactic and isotactic polypropylene. Transformation of one configuration of these polymers into another by simple rotation of units without rupture of chemical bonds is impossible.

But as a result of thermal movement of their units polymer chains may assume various conformations *, the extremes of which are a linear rigid rod and an absolutely flexible chain which tends to coil up. The chain coils up, because this decreases its surface area, and hence its free energy.

* Until recently conformational changes of polymer chains were often incorrectly referred to as configurational changes in the literature.

A disorderly coiled macromolecule is called a *random molecular coil* (Fig. 4.12). The same end-to-end distance h of a molecule may correspond to different conformations.

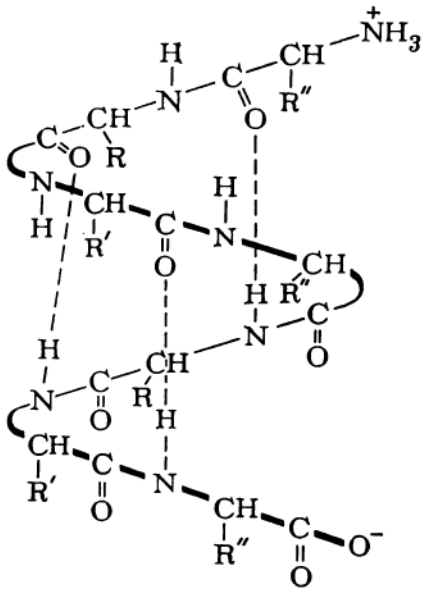


Fig. 4.14. Right-handed helix. Dashed lines indicate hydrogen bonds

If thermal motion cannot lead to the bending and coiling of a chain, the rod-shaped rigid conformation is realized (Fig. 4.13).

Finally, another type of polymer chain conformation are the helical structures detected by X-ray techniques in some solid polymers. It has been known for a long time that polypeptide chains have helical conformations in their crystalline lattices. These helices are very stable even in the dissolved state, being stabilized by hydrogen intramolecular bonds between their —NHCO groups. Figure 4.14 is a polypeptide right-handed α-helix.

It was shown recently that helical conformations are possible in vinyl

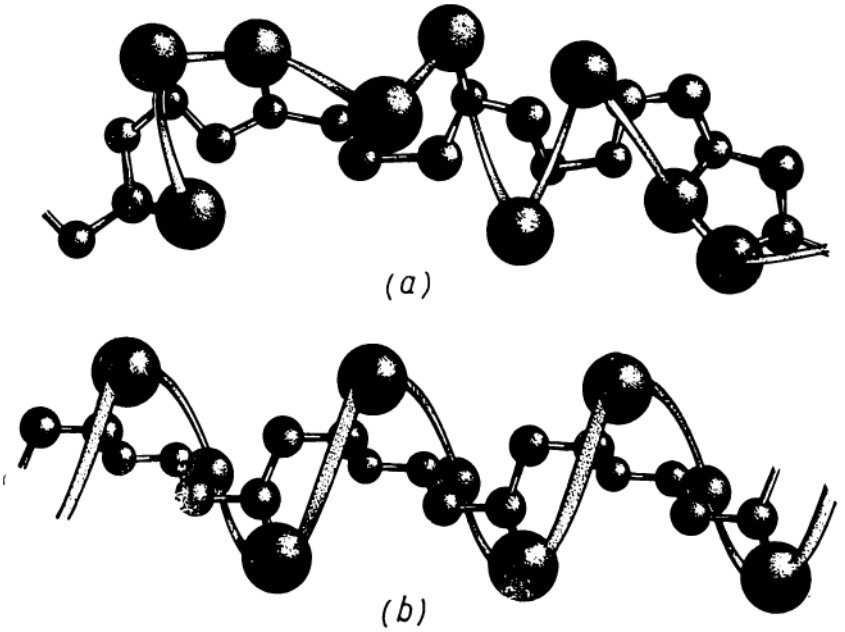


Fig. 4.15. Model of polypropylene chain:
a — atactic; *b* — isotactic

and olefin polymers as well. Here they are not strengthened by hydrogen bonds and are therefore less stable. Such helices

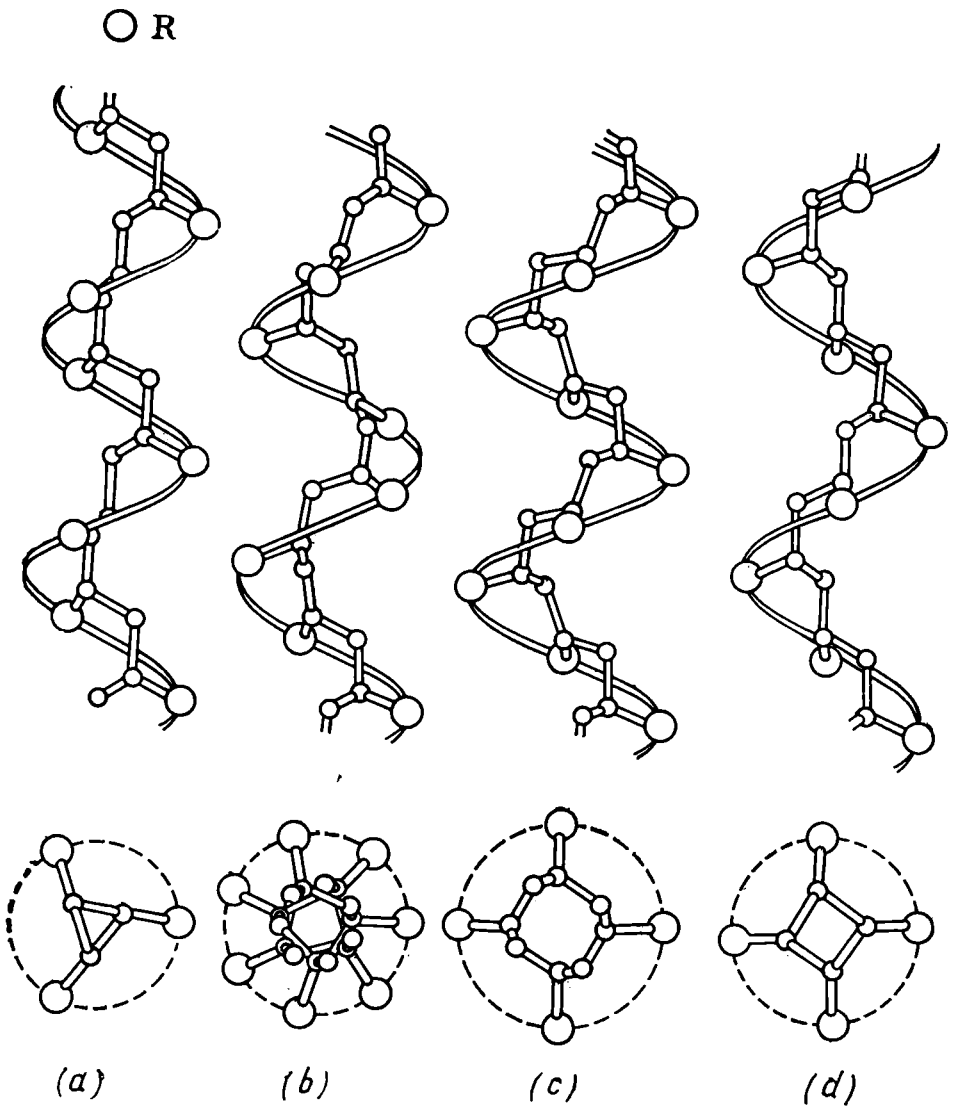
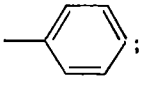


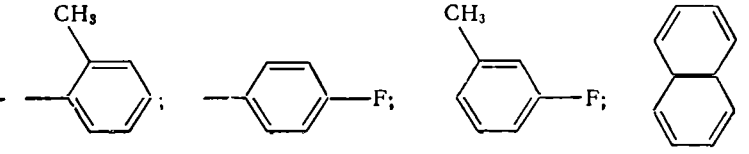
Fig. 4.16. Macroscopic models of some typical ordered helical structures of isotactic polymers:

a – R = $-CH_3$; $-C_2H_5$; $-CH_2-CH=CH(CH_3)_2$;

$-CH=CH_2$; $-O-CH_3$; $-O-CH_2-CH(CH_3)_2$;  ;

b – R = $-CH_2-CH(CH_3)C_2H_5$; $-CH_2-CH(CH_3)_2$;

c – R = $-CH(CH_3)_2$; $-C_2H_5$:

d – 

can be formed only by isotactic polymers with regular alternation of *trans-gauche* bond configuration. Since there are two *gauche* arrangements, the chain can form either a right-handed or a left-handed helix if rotation occurs always in the same direction. If the radicals are not very bulky, the helix will contain three monomer units per turn, as in the chain of polypropylene (Fig. 4.15). Atactic polypropylene cannot form a helical conformation. If large substituents are present, more space is required to accommodate them and this results in the formation of looser helices. Figure 4.16 shows possible types of helices, their diameter and pitch depending on the size and polarity of the side groups at the main chain α-carbon.

Left- and right-handed helices may form in all these cases, though these chains do not contain asymmetric carbon atoms in the usual sense of the word. The chains of many other polymers which form optically active substances contain asymmetric carbon atoms; examples are polyesters, polyamides, and polyurethanes:

Thus, an optically active poly(propylene oxide) was obtained recently.

Under certain conditions, apart from the given conformations, a polymer chain may assume the form of a globule, i.e., a spherical form. Such a conformation is characteristic of the so-called globular proteins and is found in synthetic polymers.

4.5. DIMENSIONS OF MACROMOLECULAR COILS

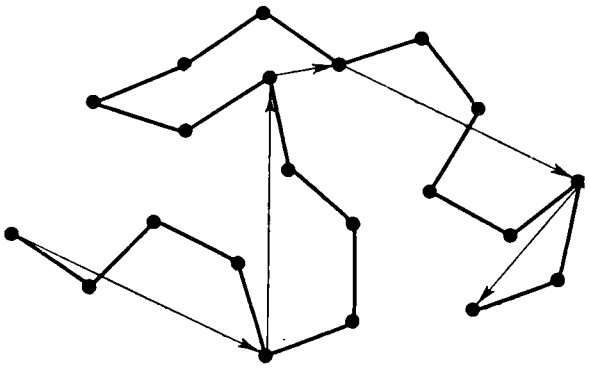
As we have already seen, a flexible chain in an isolated state assumes the conformation of a macromolecular coil (Fig. 4.12). The end-to-end distance of such a coiled chain is denoted by h. If the chain is maximally coiled, then $h = 0$; if it is maximally straightened out, then h is equal to the *hydrodynamic*, or contour, length of the chain L (Fig. 4.17). This is the length of a maximally straightened out chain without the disturbance of valence angles and bonds. The intermediate values of h may be calculated by applying the laws of statistical physics to one chain, since the number of units is very large. This calculation may be made for a freely jointed chain.

In a freely jointed chain the position of each unit is independent of that of the other units, i.e., such a chain has no correlation of arrangement. In a real chain with fixed valence angles the positions of units are interconnected. However, in a chain of very

great length there is no correlation either between the orientations of units sufficiently remote from one another. If such units are connected with lines (Fig. 4.18), the directions of these lines are independent of each other. This means that a real chain consisting of n units (each of length b) can be divided up into N independent random sections of length A.

Fig. 4.17. Model of the maximally straightened out chain

The statistical element, or segment, of chain A, whose position does not depend on the position of adjacent units, is known as the *thermodynamic segment* or the *Kuhn segment.*



Pig. 4.18. Marking off independent chain segments

Every segment consists of S monomer units; hence, the number of segments N is connected with the degree of polymerization P by the relation

$$N = \frac{P}{S} \tag{4.4}$$

The length of the segment is connected with the hydrodynamic length of the chain:

$$L = AN \tag{4.5}$$

The number of conformations that a chain may assume, or the *thermodynamic probability of a chain,* may be expressed by the Gauss formula:

$$W(h)\,dh = \left(\frac{3}{2\pi NA^2}\right)^{3/2} 4\pi e^{-\frac{3h^2}{2NA^2}} h^2\,dh \tag{4.6}$$

where h = end-to-end distance of a chain.

Graphically, this dependence is expressed by a curve in Fig. 4.19. It is clear from the graph that the maximally straightened out state ($h = L$) and the maximally coiled state ($h = 0$) are characterized by small values of W, i.e., these states have low probability.

The *most probable* end-to-end distance of a freely jointed chain h_m^2 conforms to the maximum of a curve. It may be calculated by the conditions for the maximum, i.e., the derivative $\frac{\partial W}{\partial h}$ may be equated to zero. Then, we obtain:

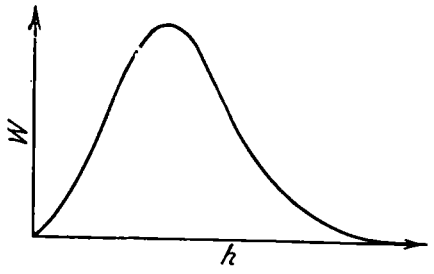


Fig. 4.19. Gaussian distribution of end-to-end distances in molecules

$$h_m^2 = \frac{2}{3} NA^2 \qquad (4.7)$$

The mean value $\bar{h}_{coil}$ and the root-mean-square value $(\bar{h}_{coil}^2)^{1/2}$ may also be calculated:

$$h_{coil} = \sqrt{\frac{8}{3\pi} NA^2} \qquad (4.8)$$

$$(\bar{h}_{coil}^2)^{1/2} = N^{1/2} \cdot A \qquad (4.9)$$

or

$$\bar{h}_{coil}^2 = NA^2$$

The size of a macromolecular coil is estimated by the root-mean-square end-to-end distance of the chains $(\bar{h}_{coil}^2)^{1/2}$ or the value of the radius of gyration $\bar{R}^2$ (rotation radius). This is the mean square of the distances of all the elements of the mass of the coiled chain from its centre of gravity. These parameters are connected by the relation:

$$(\bar{R}^2)^{1/2} = \frac{1}{6} (\bar{h}_{coil}^2)^{1/2} \qquad (4.10)$$

Both parameters are dependent on the quantity A.

The ratio of the hydrodynamic length of the chain to the root-mean-square end-to-end distance characterizes the degree of coiling of a chain:

$$\frac{L}{(\bar{h}_{coil}^2)^{1/2}} = \frac{NA}{\sqrt{NA^2}} = \sqrt{N} \qquad (4.11)$$

It follows from the equation that the coiling of the chain is the greater the larger is N, i.e., when the molecular mass of a polymer is the larger.

Coils complying with the Gaussian distribution are known as *Gaussian coils*.

4.6. THERMODYNAMIC FLEXIBILITY OF A CHAIN

To estimate the thermodynamic, or equilibrium, flexibility of a chain, its behaviour is studied in a dilute solution in the so-called θ-solvent, i.e., in a solvent which does not disturb the dimensions of a macromolecular coil.* In this case, the size of the coil turns out to be larger than that calculated by Eq. (4.9), i.e., $(\bar{h}^2_\theta)^{1/2} > > (\bar{h}^2_{coil})^{1/2}$.

The ratio of these quantities is usually denoted by

$$\sigma = \frac{(\bar{h}^2_\theta)^{1/2}}{(\bar{h}^2_{coil})^{1/2}} \tag{4.12}$$

This relation is the measure of equilibrium flexibility of a polymer chain.

However, V. N. Tsvetkov draws attention to the fact that the parameter σ may be used for estimating the flexibility of chain

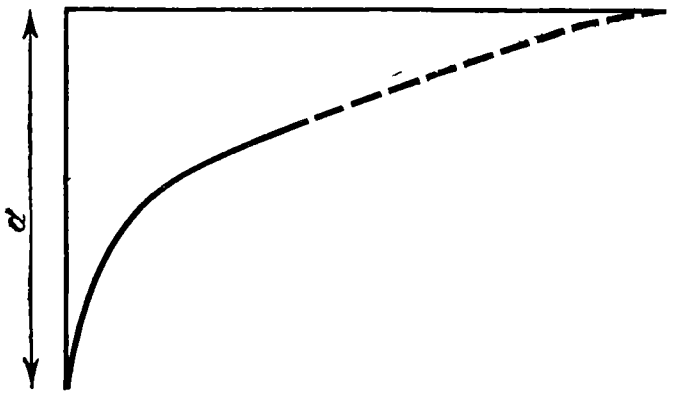


Fig. 4.20. Model of a "persistent" chain
a is persistent length

molecules, whose chain flexibility is caused by rotation around valence bonds without the deformation of valence angles. This is impossible for very many polymers (ladder polymers, polymers with rings in the skeleton of a chain, and so forth).

He believes that an effective and universal method of describing conformation properties of polymer molecules is the model of a "persistent" or "worm-like" chain, i.e., a spatial line of constant curvature (Fig. 4.20). The measure of equilibrium rigidity of such a chain is its "persistent length" *a*, which is determined by the relation

$$\overline{\cos\theta} = \exp\left(-\frac{L}{a}\right) \tag{4.13}$$

* For details on the θ-solvent, see Chap. 14.

where L = length of the segment of the worm-like chain which is bent so that the angle between the chain directions at the beginning and the end of the segment averages θ.

Hence, at $L = a$, $\theta = 67°$; therefore, a chain molecule of length a is close by its form to a poorly bent rod. When length L is sufficiently large, a worm-like chain has the conformation of the Gaussian coil, for which the length of the Kuhn segment $A = 2a$ and $\bar{h}^2 = A \cdot L$.

It follows that σ and a are connected with the value of the thermodynamic segment A, which is the most universal measure of estimating the equilibrium flexibility (rigidity) of a polymer chain.

It is necessary to clearly understand that the thermodynamic segment is not a real segment of a polymer chain. It is some *equivalent value, which is a measure of the thermodynamic flexibility of a chain.* In a maximally flexible chain, all units behave independently of one another, i.e., the length of a segment is equal to the length of a unit. *An increase in A reflects an increase in the equilibrium rigidity of a polymer chain.*

The equilibrium flexibility of a chain depends on the chemical structure of the main chain (skeleton) of a polymer and on the nature and size of the substituents (Table 4.1). Great equilibrium

TABLE 4.1. *Relative Unperturbed Dimensions of Polymer Coils in a Solution*

Polymer	$\sigma = \frac{(\bar{h}_\theta^2)^{1/2}}{(\bar{h}_{coil}^2)^{1/2}}$	Kuhn's segment $A \cdot 10^8$ cm	Number of monomers in segment S
1. Polydimethyl siloxane	1.4-1.6	14.0	4.9
2. Polymethyl methacrylate	1.8-2.2	15.1	6.0
3. Polyvinyl acetate	2.1-2.3	17.4	6.0
4. Polyisobutylene	2.2	18.3	7.3
5. Polystyrene	2.2-2.4	20.0	7.9
6. Polyethylene	2.3-2.4	20.8	8.3
7. Polypropylene	2.4	21.7	8.6
8. Cellulose trinitrate	4.2	200	20

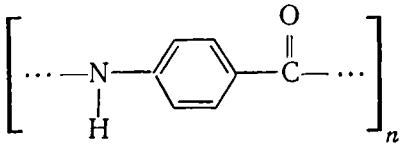
flexibility is possessed by high-molecular aliphatic hydrocarbons, ethers and esters, and amides, i.e., compounds whose chain has C—C, C—O, and N—O bonds. Such polymers are characterized by small values of $\left(\frac{\bar{h}_\theta^2}{\bar{h}_{coil}^2}\right)^{1/2}$ and Kuhn segments. The introduction of small and even polar substituents does not lead to a conside-

rable increase in these parameters. Even such a comparatively large substituent as phenyl does not produce any effect. For all polymers of the vinyl series (polystyrene, polymethyl methacrylate, polyvinyl alcohol, and so forth), the Kuhn segment is not higher than the value of 20. An increase in the dimensions of the substituents leads to a growth in the value of A. For example, for comb-like polymers (p. 37), the Kuhn segment attains the value of 50-70. Consequently, large substituents affect the rigidity of the chain, which in ordinary usage is known as skeleton rigidity. However, as Tsvetkov indicates, the skeleton equilibrium rigidity of a chain cannot be greatly changed by introducing side substituents. The equilibrium rigidity of a chain may sharply increase when there are ring formations in the chain. An example is cellulose and its esters, which have a high value of A and belong to semi-rigid polymers.

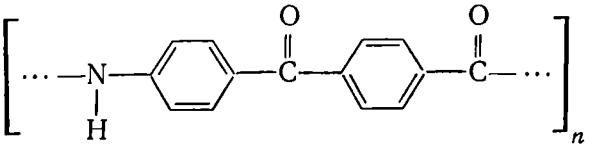
The behaviour of polyamides is very interesting. In the amide group —NH—C— itself, rotation is greatly retarted owing to the
‖
O
quasi-conjugate nature of the chains. Therefore, polyamides can have great equilibrium flexibility only if the amide groups are separated by a sufficiently large number (at least four) of methylene groups, in which rotation occurs around the C—C bonds. Therefore, aliphatic polyamides (nylon 6, nylon 6,8, etc.) have a small value of the Kuhn segment, i.e., they are flexible-chain polymers.

But the situation changes if amide groups in a chain approximate one another. In the extreme case, when the entire chain is composed of only amide groups, e.g., polyalkylisocyanates, rotation cannot occur. Such polymers have great equilibrium rigidity. Their Kuhn segment A is 500-1000.

Great equilibrium rigidity is possessed by chains of polypara-aromatic polymers, e.g., polyparabenzamide



and poly(paraphenylene terephthalamide)



This question was recently considered in detail by V. N. Tsvetkov, who, after making a thorough analysis, drew the conclusion that such macromolecules have a "crankshaft" conformation, i.e.,

the conformation of a very rigid rod whose length is proportional to the degree of polymerization.

Maximum equilibrium rigidity is possessed by macromolecules of biopolymers which have spiral conformations. Their Kuhn segment is greater than 2000.

Thus, equilibrium rigidity can vary in a very wide range, depending on the chemical structure of a macromolecule. The low value of σ, obtained when the equilibrium properties of macromolecules were being studied, does not necessarily imply that the state of rotation approximates a "truly free" one. The low value of σ can correspond to high potential barriers which hinder rotation. In addition, intermolecular interaction, which also affects chain flexibility, is of great importance. It is exhibited even in dilute solutions, when the flexibility of a chain depends on its interaction with solvent molecules (p. 346). Interchain interaction can also produce an effect. Therefore, macromolecules in bulk can possess flexibility which differs from that measured in dilute solutions. This applies, for instance, to aromatic polymers, between whose phenyl units strong interactions are exhibited. The chains of such polymers are always kinetically rigid.

4.7. KINETIC FLEXIBILITY OF A CHAIN AND FACTORS DETERMINING IT

The kinetic flexibility of a chain is exhibited in any external field; a polymer chain can uncoil to a certain extent under the action of the field applied, i.e., it can exhibit kinetic flexibility, depending on the relation between the field energy and the activation energy of the rotation barrier.

Potential rotation barrier depends on the energy of interaction of the atoms of adjacent units and consequently on the polarity of the substituents. The values of the potential barriers given on page 90 have been calculated for substances in a state of ideal gas; consequently, in the strict sense of the word, they cannot reflect the behaviour of real substances. However, they give a qualitative picture.

Hence, polymer chains which are characterized by small values of potential rotation barriers have great kinetic flexibility. This applies to:

(1) polymer hydrocarbons (polyethylene, polypropylene, polyisobutylene, and particularly polybutadiene and polyisoprene);

(2) polymers whose chains have the groupings $-C(=O)-O-C$, $-C(=O)-O-$, $-NH-C(=O)-O-$, which are separated by a large number of methylene groups (a series of polyethers and polyesters, and polyurethanes, which are synthesized on their basis);

(3) polymers whose polar substituents are arranged sparsely along the chain and do not affect the value of the potential barrier of rotation about the C—C bond, which is determined by the interaction of only the adjacent units (polychloroprene and nitrile rubbers which contain, at the most, 40 per cent of nitrile of acryiyc acid);

(4) polymers which have small substituents (—CH_3) or even large substituents but which are sparsely arranged along the chain (polyisobutylene and the copolymers of butadiene and styrene which contain, at the most, 50 per cent of the latter).

An increase in the number of polar or large substituents, or a decrease in the number of methylene groups between ethers and esters or urethane groupings, leads to an increase in the kinetic rigidity of a polymer chain. Hence, in the series of nitrile rubbers, rigidity increases as the number of the —CN substituents grows; in the series of copolymers of butadiene and styrene, rigidity increases as the styrene content grows.

Polymers whose polar or large substituents are arranged very closely along the chain have kinetically rigid chains (polyvinyl chloride, polyacrylonitrile, polyvinyl alcohol, polystyrene, and so forth), since that leads either to an increase in the potential barrier or to steric hindrances of rotation.

The presence of a small substituent, —CH_3, does not lead to a decrease in kinetic flexibility; however, if one carbon atom has two substituents (—OCH_3 and —CH_3), the chain becomes kinetically rigid (polymethyl methacrylate).

All chains of polymers with a ring structure (cellulose and its esters, aromatic polyamides, and so forth) are kinetically rigid.

The kinetic flexibility of a chain is estimated by the value of the kinetic segment, which may be determined when studying polymers in external fields (p. 224). This flexibility is expressed by values of polymer glass-transition temperatures (see p. 223). Polymers with chains of high kinetic flexibility have low glass-transition temperatures, which range from —40 °C to —70 °C. At ordinary temperatures, they are rubber-like materials. Polymers with a mean value of kinetic rigidity of chains have glass-transition temperatures of 80-100 °C. Very rigid chain polymers are characterized by very high glass-transition temperatures, being above 200 °C.

It follows that thermodynamic and kinetic flexibilities of the most flexible-chain polymers and those of the most rigid-chain polymers coincide, i.e., the former have small values of thermodynamic and kinetic segments, while both of these parameters of the latter are large.

In intermediate cases (polystyrene, polyvinyl chloride, polyacrylonitrile, polymethyl methacrylate, and so forth), kinetic flexibility

and thermodynamic flexibility do not coincide. All the said polymers have high thermodynamic flexibility and low kinetic flexibility.

Molecular mass. As we have already seen, internal rotation is manifested also in low-molecular substances. Therefore, flexibility is said to be possessed by the molecules of low-molecular aliphatic hydrocarbons and aliphatic alcohols, which have large alkyl radicals. The greater the ability of a compound to undergo rotational isomerism, the smaller is the molecular mass M, beginning with which the equilibrium flexibility of a chain is manifested, i.e., the smaller is the value of the thermodynamic segment A. At $M > A$, the equilibrium flexibility of a chain of flexible-chain polymers does not change with a further increase in the molecular mass.

A different picture is observed in respect of rigid-chain polymers: when the values of M are small, an oligomer molecule has the conformation of a rigid rod; at very high molecular masses, its conformation corresponds to the Gaussian coils.

Molecular mass also does not affect the value of the potential rotation barrier, since it is determined only by interaction between adjacent units. Therefore, the kinetic flexibility of a chain, beginning with the molecular mass equal to the value of the kinetic segment, also does not depend on molecular mass. However, the larger is the molecular mass of a polymer, the greater is the number of possible conformations which a chain may assume. Therefore, the degree of its coiling increases, and such a chain is capable of deforming to a great extent in external fields.

Spatial network. The presence of chemical bonds between chains limits their mobility. If, on the average, there are two chains per crosslink, the chain as a whole cannot move at all, but the units do so. In the presence of a sparse network, when the molecular mass between its points is $M_{net} \gg A$, network density does not affect chain flexibility. If network density is such that M_{net} becomes smaller than the value of a thermodynamic segment, $M_{net} < A$, an increase in the number of crosslinks leads to a sharp limitation of chain flexibility.

Temperature. Temperature has a comparatively small effect on intra- and intermolecular interactions. The only type of interaction which depends on temperature is dipole-dipole, or orientation, interaction (p. 93). Therefore, a change in temperature virtually does not affect either the value of the potential rotation barrier U_0 or the value ΔU. However, as temperature rises, the kinetic energy of a molecule increases, and then there is great opportunity for overcoming the potential barrier; the rotation rate of units and the intensity of their torsional oscillation increase, and equilibrium flexibility and kinetic flexibility grow.

4.8. PRACTICAL IMPORTANCE OF CHAIN FLEXIBILITY

Chain flexibility is one of the main features on the basis of which polymers can be divided into two large groups: elastomers or rubber-like polymers and plastics.

The term *elastomers* is usually used to denote polymers with very flexible chains (at room temperature). Polymers whose chains are stiff at room temperature are called *plastics*. Of course, this division is arbitrary, since the kinetic flexibility of a chain depends on temperature. For example, plastics may become elastomers when heated [poly(vinyl chloride), polystyrene, etc.], while elastomers change into solid plastics if the temperature is lowered. The arbitrariness of such a division is still more pronounced in polymers which may be either plastic or rubber-like at room temperature. These polymers have flexible chains and hence crystallize readily. They are plastics in the crystalline state and elastomers in the amorphous.

The effect of crystalline structure on the properties of polymers is discussed in the following chapters.

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CHAPTER 5

Supermolecular Structure of Polymers

The molecular structure of a polymeric substance (chemical constitution), i.e., its chemical composition and way of linking together atoms in a molecule, does not unumbiguously determine the behaviour of a body made out of these macromolecules. The properties of such a body depend also on its supermolecular (physical) structure. This term implies the way of macromolecular chain packing in spatially separable elements out of which macroscopic bodies are made, the dimensions and shape of these elements and the arrangement of many such elements relative to one another.

The concept of the supermolecular structure of a matter originated at the start of the modern technology of materials when the dependence of properties of metals on the regime of their thermal treatment was revealed, and then it continuously developed and spread to other classes of materials, including high-molecular compounds. The first, purely theoretical principles and models were replaced by more realistic ones, based on direct experiments and measurements, which, owing especially to the works by V. A. Kargin and his coworkers and also A. Keller, E. Fischer and others, now constitute a clear concept of the diversity of forms of the supermolecular structure of polymers and its determining role in the appearance of a large set of diverse physical and mechanical properties of high-molecular compounds.

Structural processes developing in various materials were understood, and the shape, dimensions and relative arrangement of the elements of a supermolecular structure were ascertained only owing to the development of direct physical methods of investigation.

5.1. METHODS OF INVESTIGATION OF POLYMER STRUCTURE

The physical structure of a substance is studied by means of electromagnetic vibration of various wavelength. There are "visual" and interference-diffraction methods in this respect. Visual methods are based on the use of vibrations having a wavelength λ which is far smaller than the dimensions of the structural element under consideration. In this case, a researcher sees every element and distinguishes its form, boundaries and the specific features of its structure whose dimensions are also greater than λ. Visual methods of investigation include optical and electron microscopies.

Interference-diffraction methods make it possible to estimate the mutual arrangement of a large number (ensemble) of ordered particles (elements). They are based on the use of electromagnetic vibrations whose wavelength is of the same order as or much larger than the characteristic size of the structural element under consideration. In this case, a researcher sees either the diffraction pattern of electromagnetic waves on separate objects or the interference pattern of waves diffracted on an ordered ensemble of scattering centres. In the first case, the shape and dimensions of the object on which scattering is taking place can be determined. In the second case, it is possible to determine the distance between scattering centres, i.e., the repeating distance, because the character of interference is caused by a certain periodic structure with spatially-changing transmissivity relative to electromagnetic vibrations. Interference-diffraction methods consist of: small-angle and large-angle X-ray diffraction, electron diffraction, neutron diffraction and light scattering.

By varying the wavelength in a wide range when realizing both groups of methods, information can be obtained on the features and character of arrangement of the structural elements of a matter whose dimensions range from units of microns to several millimetres.

An independent group of methods for studying the structure of a body consists of integral methods, which are based on the measurement of the dependence of any physical property of a body on its structure. Such methods are: thermal (measurements of the heat capacity and transition temperatures, differential thermal analysis, thermal effects of dilution, etc.), mechanical (measurements of limiting, deformational and relaxational properties), electric (electric permeability, dielectric losses, electric conductance, etc.) and dilatometric (measurements of density and its change with time) methods. They include also the methods of absorption (reflecting) electromagnetic vibrations, which are connected with the interaction between radiation and chemical bonds in a sub-

stance (special methods of infra-red spectroscopy, particularly infra-red dichroism, and also similar methods with the use of other frequencies). Some of these methods, being indirect ones for studying polymer structures, are considered in other chapters of the book, while others are not considered at all because they relate to very special problems.

5.1.1. Light (Optical) Microscopy

In this method, an object is examined in optical microscope in transmitted or reflected light and a magnified image of the object is formed in the plane of image formation of the objective lens. An ordinary observation of polymer samples in an optical microscope in transmitted nonpolarized light gives little information owing to the small difference in the optical densities of various structural elements. Polarized light produces much better results, because the crystallization and orientation of polymers cause the birefringence effect (p. 132).

The wavelength of visible light is 0.4-0.8 μm. Therefore, optical methods make it possible to discern structural elements whose dimensions range from several to many hundreds of microns. The resolving power, i.e., the minimum distance between two points of an object that can still be seen separately on an image formed in the light microscope, is 1-0.5 μm.

In optical microscopy, objects to be examined usually do not have to be specially prepared. Samples in the form of thin films or slices from bulky blocks whose thickness ranges from several to hundreds of microns are the most convenient for investigation in transmitted light. Optical microscopy in reflected light is widely used for studying the structure of the surface of bulky polymer bodies and the rupture surface.

The methods of optical microscopy make it possible to visually describe and represent the character of structural formations in crystalline polymers in the appropriate range of dimensions. They are widely used for observing structural transformations in crystallization, studying the kinetics of this process, controlling the macroscopic structure of a body obtained under different technical conditions, and observing structural transformations under the action of various effects (deformational, heat, etc.).

5.1.2. Electron Microscopy

In electron microscopes, the radiation source is the cathode, which emits an electron beam (an electron ray). Vibrations with a definite wavelength, which depends on accelerating potential, correspond to the translation of electrons in space. Modern com-

mercial electron microscopes, which operate at accelerating potential of 40-150 kV,* create electron beams accompanied with the propagation of electromagnetic vibrations having a wavelength of 0.06-0.03 Å. Thus, they make it possible to study structural elements whose dimensions range from several angstroms to a few microns. The resolving power of electron microscopes is several angstroms (usually 3-20 Å), and magnification varies between 3×10^3 and 10^5.

Like in the light microscope, the magnified image of an object is formed in the electron microscope, but it cannot be regarded in the ordinary sense of the word as a photograph made by an ordinary camera. To interpret the electron-microscope micrographs ("images") correctly, it is necessary to know the laws of interaction between an electron beam and a substance.

In electron microscopy, there are definite restrictions on objects to be examined and definite requirements for the preparation of samples for examination. To begin with, the thickness of the transmitting layer is confined on the average to 1000 Å owing to the strong interaction between the electrons and the substance being examined at relevant accelerating potentials. But, in practice, even thinner samples are examined. The methods of electron microscopy make it possible to study the structure in very thin films and sections of polymers or the structure of the surfaces of bulk materials, or rupture surfaces by the replication techniques, i.e., transparent prints from the surface of the sample being examined.

The contrast on micrographs is connected with the different scattering ability of the nuclei of various atoms with respect to the electron beam. Atoms of heavy metals scatter electrons to the greatest extent. Therefore, the contrast of polymer objects is often intensified by shadowing them with heavy metals, such as chromium, palladium, gold and platinum.

An important factor which restricts the method of electron microscopy is its statistical character, connected with the possibility of significant errors (artefacts) in the determination of the structure, which are due to difficulties of preparing polymer objects.

Scanning electron microscopes are deprived of a part of these disadvantages, and they are being used now on an ever wider scale. An important advantage of such a microscope is that it excludes the stage of the complicated preparation of samples. In the microscope, the object is illuminated by an almost parallel electron beam of a small diameter. The intensity of electron scattering is controlled by Geiger counters. The electric circuit transforms the scattered electron beam into the cathode-ray beam whose

* Electron microscopes having an accelerating potential of 200, 500, 1000 and even 3000 kV are now being industrially produced.

intensity varies accordingly, and an image of the sample, whose magnification can be changed within a wide range, is formed on a screen. The maximum resolving power of a stereoscanning microscope is determined mainly by the diameter of the beam, which is usually about 300 Å *, i.e., an order lower than that in a transmission electron microscope. This method makes it possible to clearly show the structure of the surface of bulky samples or chips.

5.1.3. X-Raying

If the size of structural elements is far smaller than the wavelength λ of electromagnetic radiation used for investigation and these elements form an ordered ensemble with characteristic distances d between them (known also as interplanar distances)

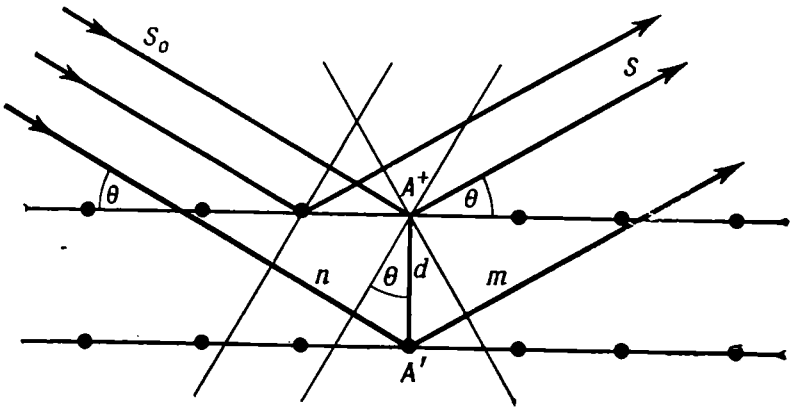


Fig. 5.1. Diagram of the reflection of rays on an one-dimensional structure with period d. S_0—incident rays; S—diffracted rays. The propagation difference of the rays reflected from two planes is $nA' + mA' = 2d \sin\theta$. The angle between incident and diffracted rays is 2θ

that are commensurable with λ, an observer sees interference pattern of diffracted rays, which makes it possible to determine the mutual arrangement of structural elements, but not their own dimensions.

The wavelength of X-ray radiation is approximately 0.1-100 Å. The wavelength depends on the material out of which the anticathode of the X-ray tube is made. In practice, an anticathode made of copper is most widely used for investigating polymers. The nickel filter picks out of emitted radiation the K_α line to which the wavelength of 1.54 Å corresponds.

* There are stereoscanning microscopes with a beam diameter of 100, 50 and even 20 Å. According to reports, devices with a beam diameter of 3 Å are being worked out.

The theory of X-raying is based on the Huygens-Fresnel hypothesis, according to which every point reached by electromagnetic vibrations may be regarded as a radiation centre. Figure 5.1 illustrates how this principle is used to explain the diffraction and interference of parallel rays; it shows one-dimensional structure (e.g., the section of a diffraction grating by the diagram plane) on which a parallel beam of rays is incident. Each point shown in the diagram is regarded as a source of vibrations which interfere in the screen plane. There are points whose position is characterized by the angle θ between the direction of the incident ray and the reflecting plane, and in which the intensity of the interference of rays diffracted at all the structural points is maximum. Angle θ is calculated by the Woulfe-Bragg formula:

$$2d \sin \theta = n\lambda$$

where d = period of a one-dimensional structure
λ = wavelength of incident light
n = integers (equal to 1, 2, 3, etc.) known as the reflection order.

There is a number of values of θ determined by the values of n in which the intensity of the rays being diffracted is maximum. Diffracted X-rays are detected either by their action on a photographic film (plate) or by means of any radiation detector, say a Geiger-Müller counter. When use is made of the photographic technique of registration on a special X-ray film, the place where diffracted rays are incident on it blackens (this blackening is known as reflex) and its position is determined by the Woulfe-Bragg condition. Thus, diffraction on an one-dimensional structure, such as the diffraction grating, causes the appearance of a series of parallel lines whose position is determined by the angle θ.

If diffraction is effected on a two-dimensional (plane) grating with scattering at its points, the distance between which in one direction is a and, in another, b, the direction of the diffracted ray of maximum intensity is ascertained by a system of two Woulfe-Bragg equations, which determine diffraction conditions:

$$2a \sin \theta_1 = n\lambda$$

$$2b \sin \theta_2 = m\lambda$$

and the diffraction pattern consists of a system of spots, the direction towards which with respect to the direction of the incident beam is determined by the values of two angles θ_1 and θ_2.

For a three-dimensional grating with periods a, b and c in each direction, whose role in the body under consideration is played by

its crystalline lattice, three diffraction conditions which determine the values of three angles θ_1, θ_2 and θ_3 must be met:

$$2a \sin \theta_1 = n\lambda$$
$$2b \sin \theta_2 = m\lambda$$
$$2c \sin \theta_3 = k\lambda$$

where n, m and k are integers which give the diffraction order. But three angles in space cannot be selected arbitrarily because the angles between the arbitrary line and three mutually perpendicular coordinate axes a, b and c are connected by the geometric condition $\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 = 1$. The given four equations, known as Laue's equations, can be solved (i.e., from them, the angles θ_1, θ_2 and θ_3 for a grating with preset parameters of a, b, and c can be found) not for any wavelengths. Thus, unlike diffraction on one-dimensional and plane structures, diffraction on a three-dimensional grating gives maxima not for all wavelengths, but only for strictly definite ones which ensure the compatibility of the system of the four equations; the rest of the waves are scattered in all directions without producing maxima.

The foregoing formulas make it possible, in principle, to calculate the values of period d. For example, if monochromatic radiation with a known wavelength λ is used and the directions of θ in which the intensity of scattered radiation is maximum are determined experimentally, period d is easily found by the Woulfe-Bragg formula.

The structural ordering of the arrangement of macromolecules and their parts leads to several types of periodicity which are characterized by their dimensions (the value of the period). In polymers, there are three basic types of ordering: the small period, the helical pitch (repeat distance along the chain) and the large period.

The small period characterizes the dimensions of the elementary crystalline lattice (see further), i.e., of the smallest structural elements (bricks) out of which all polycrystalline bodies are made in their various combinations.

It was noted earlier (see. p. 98) that regularly built macromolecular chains with side substitutes assume in space, due to energy, helical conformations with constant pitch. The helical pitch conforms to the periodicity along the chain with a specific size of the order of several tens of angstroms that is a peculiar characteristic of a macromolecule of a given chemical composition.

A special type of ordering inherent only to polymer bodies is characterized by the alternation of the regions of long-range and short-range orders and, in the limit, amorphous and crystalline regions along the chains in a partially crystalline and, especially,

in oriented polymer. The so-called "large periods" which appear in this case have the order of hundreds of angstroms.

The three types of periodicity of a polymer structure have their own characteristic values of angles θ in which maxima of scattering are to be expected. For a small period and a helical pitch ranging from one to twenty angstroms, the values of the Bragg angles range from several degrees to some tens of degrees. In this case, we usually speak of large-angle X-ray scattering.

In investigating the large period, when the values of d reach hundreds of angstroms, in order to find the position of maxima, it is necessary to measure the angular intensity of scattering in the range of angles from several minutes to 1-2°. Accordingly, in this case, we speak of small-angle X-ray scattering *.

Methodically, X-raying is performed according to one of the three basic variants.

(1) Laue's method is used for studying single-crystals of sufficiently large dimensions (above one millimetre). In this method, use is made of a beam of polychromatic ("white") X-rays that always has such a wavelength for which Laue's four equations written above are satisfied simultaneously. The X-ray pattern obtained represents a system of spots ("point reflexes") from various systems of planes in a crystal. This method is practically not used for studying polymers, because polymer single-crystals of a sufficiently large size could not be obtained.

(2) According to Braggs' method, monochromatic radiation is used to study a single-crystal, while the theoretical principles of diffraction are effectuated by rotating the sample or tilting it when it is being photographed. The photographic film on which diffracted rays fall is arranged on the surface of a cylinder around a sample which is placed along the cylinder axis. Diffraction maxima appear whenever, in the course of rotation, the directions of crystallographic planes form with the direction of the incident ray the angle θ determined by the Woulfe-Bragg equation.

(3) According to the Debye-Scherrer method, whose scheme is given in Fig. 5.2, samples in the form of powder (for this reason, this method is often known as the "powder" method) or of a polycrystalline body are examined and monochromatic X-rays are used. The incident monochromatic ray is diffracted on the planes of the crystallites of a polycrystalline sample that satisfy the Woulfe-Bragg equation by their orientation with respect to the incident ray. Diffracted rays will spread along the *generatrices* of a cone with the vertex angle equal to 2θ. The intersection of

* The following example is indicative in this respect: if $d = 100$ Å, it follows from the Woulfe-Bragg formula for $\lambda = 1.54$ Å that the maxima of scattering intensity will appear at the angle $\theta = \arcsin 1.54/100 \times 2$, i.e., at angles of 26.5′.

these cones with the flat photographic film, which is perpendicular to the incident ray behind the sample, produces a system of concentric rings of growing radii, each of which contains all the reflections with the same angle θ: a powder X-ray pattern (Fig. 5.3 upper). Two arcs, symmetrical with respect to the primary ray, are produced from each cone on the cylindrical film, whose axis is perpendicular to the incident (primary) X-ray. Such a X-ray pattern is known as the Debye powder pattern.

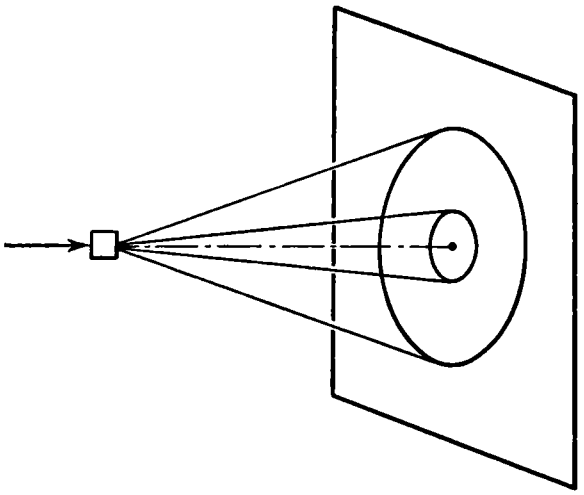


Fig. 5.2. Diagram of the formation of a powder X-ray photograph on sheet film

The Debye-Scherrer method is of the greatest importance to the study of the structure of polymeric bodies. In particular, it is widely used for investigation of oriented polycrystalline samples. In the course of extention, crystals are oriented in a definite way with respect to the axis of strain. Therefore, a texture appears on the X-ray pattern of oriented samples: rings degenerate into arcs of various lengths. Such diffraction patterns are known as texture patterns (an example is given in Fig. 5.4). The distribution of intensity along the arc characterizes the degree of orientation of crystallites relative to the axis of tension. Of the greatest importance in invesigating polymers are the texture patterns of the maximally oriented samples, when all the crystals are oriented by the same axis (usually axis *c* of a crystalline cell) along the direction of tension, creating the axial texture, and X-ray patterns of such samples are similar to point ones. It is these X-ray patterns which are usually used to determine the type and parameters of the unit crystalline cell and the repeat distance along a chain.

X-ray patterns are usually quantitatively processed by the trial and error method, setting a hypothetical structure of a substance, calculating a diffraction pattern which is expected for it and com-

paring it with the X-ray pattern being observed experimentally. Then, if need be, another hypothetical model is chosen and calculations are made again until the calculated and observed scattering patterns coincide satisfactorily. This method is successful, because high-speed electronic computers are now used for structure

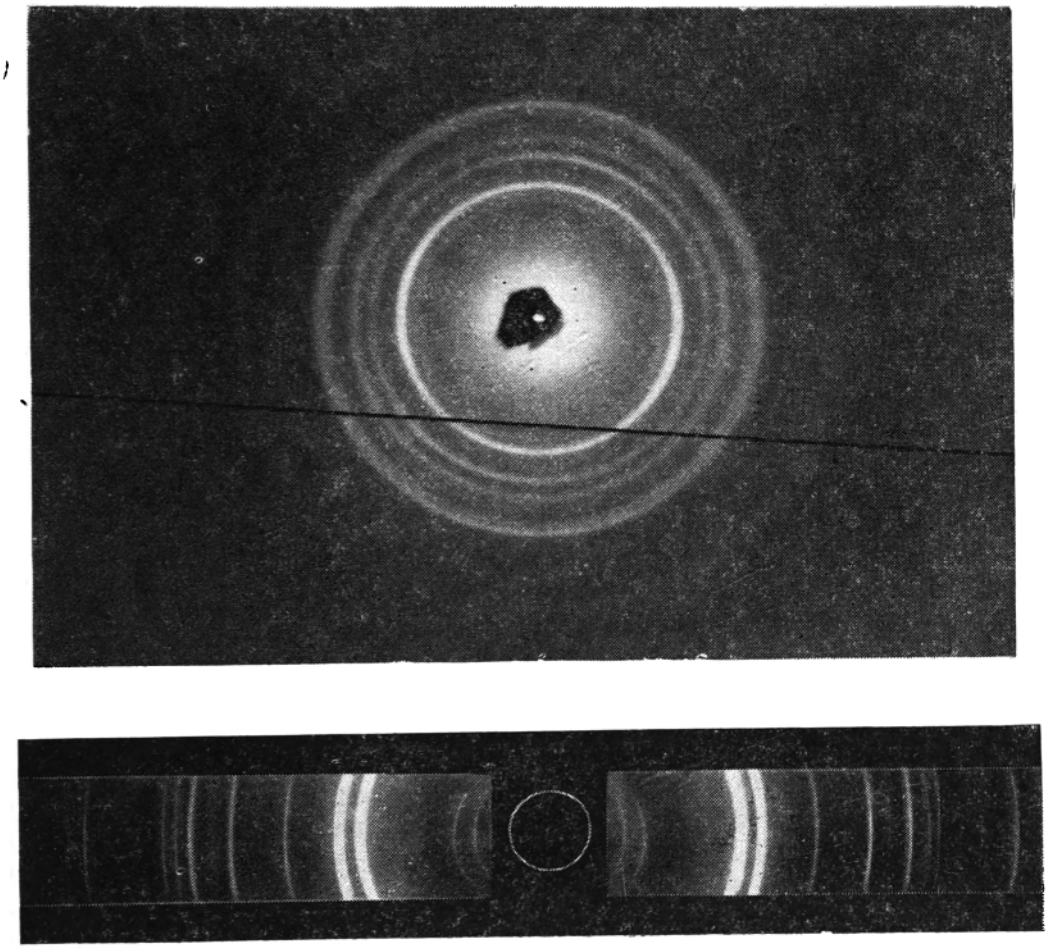


Fig. 5.3. (upper) X-ray photograph of polypropylene obtained by the Debye-Scherrer method on sheet film; (lower) Debye powder pattern

analysis in the laboratory. It is especially important in deciphering the conformation structure of polymers and especially of natural polymeric compounds. In this way, such great successes of the X-raying of polymers as the determination of the conformation of the desoxyribonucleic acid chain were recently made.

X-ray diffraction analysis makes it possible both to obtain much information on the structure of polymeric bodies and its change as a result of heat, mechanical and other effects, and on the phase transformations of a substance, and to determine the conformation

of chains, the character of orientation of crystallographic and molecular axes in a crystalline cell and their change caused by external effects. The X-ray method makes it possible to determine average dimensions of crystals and their distribution according to dimensions, the deffectness of crystalline structure, and so forth. Small-angle X-ray scattering gives grounds for forming opinions on the magnitude of a large period and its change under various

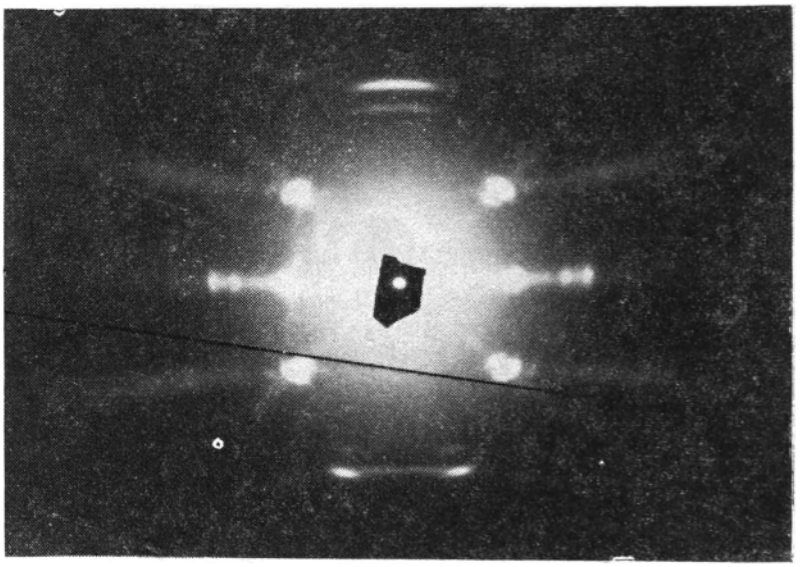


Fig. 5.4. X-ray texture pattern of polypropylene on sheet film

thermomechanical actions, and on the state (density) of amorphous layers, and also makes it possible to register the origination of tiniest (submicroscopic, up to 10-100 Å) cracks in polymeric bodies. The X-ray methods are especially advantageous because they do not require the special preparation of objects and make it possible to study the polymer structure and its transformation directly under the action of external fields, particularly heat and mechanical loads.

5.1.4. Electron Diffraction

The principles of using electron diffraction for studying polymers practically do not differ at all from those of X-ray diffraction. But since the wavelengths λ of electrons are smaller than that of X-rays, the electron diffraction method makes it possible to obtain clear electron-diffraction patterns on small samples (or from small regions of a sample) and with short exposures. Electrons are intensively absorbed by a substance, and therefore electron-diffraction investigations are performed under high vacuum, while

samples are made in the form of fine films or the method is used to study the structure of thin surface layers of a substance. In addition, account must be taken of the fact that the electron flow may cause structural transformations of polymers; in particular, it may upset order and sometimes destroy macromolecules with the formation of macroradicals (p. 67).

5.1.5. Neutron Diffraction

The neutron-diffraction method is based on the effect of scattering a flow of slow neutrons by the atomic nuclei of a substance. Contrast appears owing to the difference in the intensity of scattering a monochromatic neutron flow on the nuclei of diverse mass, and an important fact is that, unlike X-rays and electrons, neutron flow does not carry an electric charge and, consequently, the intensity of neutron scattering is determined only by the mass of the nucleus. In practice, the neutron-diffraction method is used by comparing the intensity of scattering on the nuclei of hydrogen and deuterium when investigating a system which has a certain amount of deuterated molecules in the medium of hydrogen-containing chains or vice versa. Contrast in this case is especially great owing to the double change in the mass being scattered. Nuclear reactors are usually the source of neutron flow. The wavelength of the flow depends on neutron energy; the values of λ equal to 1.6-1.8 Å correspond to the temperature range of 20-100 °C. Cold neutrons are used to obtain beams with wavelengths reaching 10 Å. At present, an important field of neutron diffraction is the estimation of conformations of macromolecules in a solid glassy state of a polymer. In this case, two variants are methodically possible: either the polymer or the matrix is deuterated. The theory of processing the results of such observations coincides with that of scattering light on chain macromolecules in dilute solutions, a method which is also used to determine chain conformations.

5.1.6. Small-Angle Polarized Light Scattering

In this method, proposed by R. Stein and developed by S. Ya. Frenkel in the Soviet Union, polarized light is used. The method consists in the consideration of the theory of scattering on bodies of the simplest geometric form (disc, sphere, rod, ellipsoid, etc.) and in a comparison of the pattern of experimental distribution of scattering intensity with the theoretically predicted one. The coincidence of the pattern observed with one of the theoretically possible patterns is used as a basis both for forming the opinion that the geometric shape of the element being scattered is truly similar to that of one of the simplest models and for de-

termining its dimensions. This method is used for observation the kinetics of the origination, growth and disintegration of structural elements whose size is of the order of 1 μm and for watching the mutual transformation of structures, such as when a transition is being made from spherical to elongated structural elements as polymers are deformed.

5.2. STRUCTURE OF CRYSTALLINE POLYMERS

The physical structure of a body is estimated at first by relating it to the class of crystalline or amorphous bodies which do not have a crystalline lattice. This is usually done by X-ray analysis. As we have seen, the X-ray pattern of a crystalline polymer (see

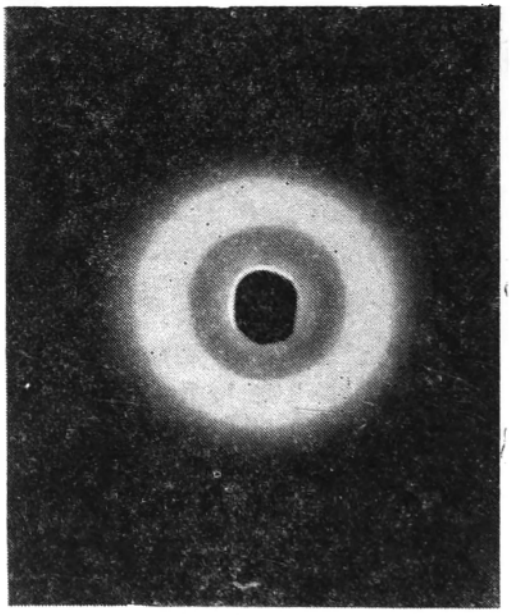


Fig. 5.5. X-ray photograph of an amorphous polymer

Fig. 5.3) contains a certain number of concentric rings which are rather clearly defined. In the X-ray pattern of an amorphous polymer one or two (rarely more) diffuse rings, the so-called amorphous halo, appear (Fig. 5.5).

An extreme case of the ordering of crystalline polymers is the formation of ideal crystalline bodies, single-crystals, in which the relative arrangement of atoms is strictly the same throughout the volume. All real bodies have a certain number of distortions of the strictly ordered arrangement of the simplest structural elements in the form of dislocations, various defects, and so forth. In polymers, deviations from ordered arrangement may be caused either by disturbances in the strict regularity of the chain structure or by the fact that the binding of atoms into a single long chain

hinders their free diffusion, which is necessary for forming an ideal crystal. Therefore, regions of greater and smaller ordering always alternate in polymers. Since these regions cannot be separated from one another because the same macromolecular chains are in them, they do not form separate phases, and the entire structure of a crystalline polymer can be interpreted as a very imperfect crystal or as a complex combination of crystalline and amorphous regions which are ordered to a different extent. Therefore, X-ray patterns of crystalline polymers always have a broad amorphous halo together with clear ring-shaped reflexes (see Fig. 5.3).

The term "degree of crystallinity" is often used as a quantitative characteristic of the degree of ordering of an amorphous-crystalline polymer, and it is determined by the following formula:

$$C = C_{am}(1 - x) + C_{cr}x$$

where C = index of a certain property of a body that is being measured

C_{am} and C_{cr} = values of this parameter for a purely amorphous body and a purely crystalline one

x = share of crystalline body.

Hence the degree of crystallinity of a body

$$Cr\% = 100x = \frac{C - C_{am}}{C_{cr} - C_{am}} \times 100$$

the letter C may stand for very diverse quantities, such as density, the intensity of lines in an infra-red spectrum or reflexes on an X-ray pattern, and transparency. The estimates of the degree of crystallinity that are obtained by different methods in general do not coincide. Therefore, the term degree of crystallinity is ambiguous and does not have a strict physical meaning. It represents a certain integral averaged estimate of the structure of a body. Nevertheless, as a primary estimate of the specific features of the structure of a polymer, and also in comparative tests of the same polymer with a different prehistory, this characteristic may be, in some cases, a useful characteristic of the properties of a body.

A complete characterization of the structure of a substance is based on a detailed description of its morphology, i.e., the totality of the structural formations observed, their forms and boundaries, and their mutual arrangement and hierarchy (the way of building complex formations from simple ones). Among the main morphological forms of crystalline polymers are various single-crystals (lamellar, fibrillar, globular) and spherulites. Intermediate morphological formations are also sometimes singled out owing to a continuity of the transition between various structural forms.

5.2.1. Crystallographic Cells in Polymers

The simplest element of the structure of a crystalline polymer is its crystalline cell formed by several atoms (parts of chains). It is characterized by strictly definite dimensions, i.e., by distances between atoms or periods (parameters) of the lattice a, b, c and angles α, β, γ between planes on which the atoms lie. Crystalline cells in polymers in essence do not differ at all from cells formed by low-molecular compounds. In particular, they obey all the rules

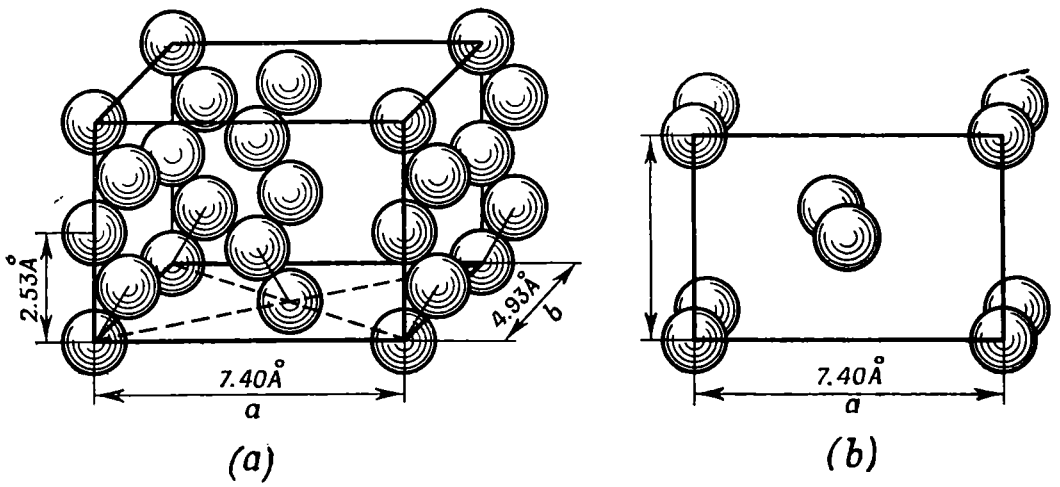


Fig. 5.6. Conformation of a chain (*a*) and the arrangement of chains in a crystalline cell of polyethylene (*b*)

of symmetry which have been elaborated for low-molecular crystals, and they are described by the same characteristics as those of any other ordered arrangements of elements in space.*

A typical example of a crystalline cell formed in polymers is the orthorhombic spatial unit cell of polyethylene represented in Fig. 5.6. The dimensions (parameters) of the unit cell that are determined by X-ray method are:

$$a = 7.40\,\text{Å}, \quad b = 4.93\,\text{Å}, \quad c = 2.53\,\text{Å}$$

The density of a crystal that corresponds to these dimensions is 1.00 g/cm^3.

The chains of polyethylene, like those of any *n*-paraffins, are in a crystalline cell in the form of a planar zig-zag (Fig. 5.6*a*) where all carbon atoms are arranged on the same plane. In an unit orthorhombic polyethylene cell, chains are arranged along four edges and in the centre of the cell.

* There are, in all, seven types of symmetry of crystalline systems to which 14 various types of Bravais lattice belong, i.e., 14 possibilities of the mutual arrangement of atoms with strict spatial periodicity being maintained.

Crystalline cells of any crystallizing polymers can be described in a similar way. However, unlike polyethylene, linear chains with bulky side substitutes are characterized not by a planar zig-zag conformation, but by a helical conformation of macromolecules which are in a crystal (see p. 98). One helical loop may contain a different number of monomeric units, depending on the nature of a polymer, and therefore the parameters of unit cells may vary in a very wide range.

Like low-molecular compounds, polymers are characterized by polymorphism, according to which the same substance may crystallize into various forms. For example, polypropylene may form crystals which belong to monoclinic, hexagonal and triclinic types of symmetry. Transitions between various polymorphous formations occur either upon a change in temperature, and in this case they are usually typical first-order phase transitions, or under the action of a load, which leads to a jumpwise or gradual change in the parameters of a crystalline cell.

A crystalline cell is the primary element of the structure of any crystalline polymer. The mutual arrangement of unit cells gives rise to various higher structural forms within the limits of the crystalline state of a body, that determine the morphology of a crystalline polymer.

5.2.2. Single-Crystals

If a macroscopic body consists entirely of unit cells, all of which can be made to coincide with one another by translation alone, i.e., by parallel transfer along edges at distances equal to periods in the appropriate directions, it implies that, by its physical structure, the body is a single-crystal (i.e., an ideal crystal). The ability of high-molecular compounds to form monocrystals was first ascertained in 1957 independently by Fischer, Teil and Keller. In reality, polymer single-crystals always contain a certain number of defects which originate when chains are being packed. However, these defects are insignificant.

5.2.3. Lamellar Single-Crystals

Polymer single-crystals are usually grown by crystallizing a polymer from dilute solutions (the concentration of a polymer is usually less than 1 per cent) on gradual cooling or isothermal aging under the equilibrium temperature of dilution. The outward appearance of a single-crystal (dimensions, shape, regularity of structure) depends on the chemical structure of a chain and crystallization conditions (temperature, concentration of a solution, the nature of a solvent, the cooling rate, etc.). Polymer single-

crystals in their simplest form are mono-layer flat plane, lamella which are often rhomboid (Fig. 5.7) with the following typical dimensions (by the order of their values): thickness is 100 Å, and the size of a plate up to 1 μm. The axes *a* and *b* of a crystalline cell correspond to the long and short diagonals of a rhomb, while axis *c*. along which macromolecular chains are directed, is perpendicular to the crystal plane.

Since the length of macromolecules constitutes tens of thousands of angstroms, while the thickness of a crystal is not more than 200 Å, a chain cannot fit into a crystal perpendicular to its larger plane otherwise than by turning on its surface by 180°, i.e., the

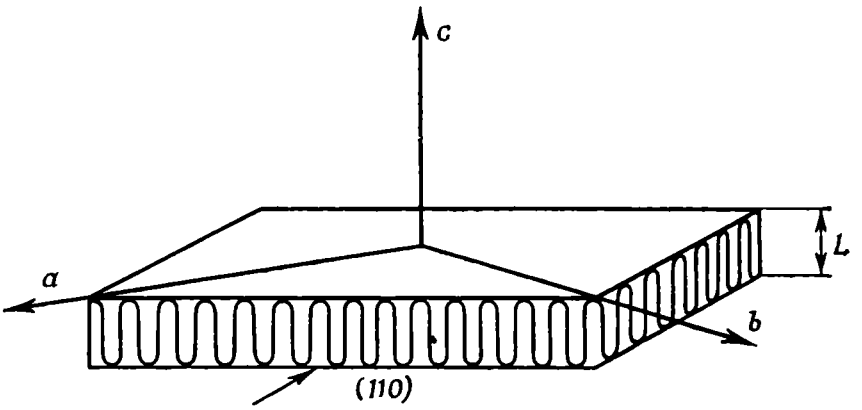


Fig. 5.7. Diagram of the arrangement of crystallographic axes in a lamellar crystal of polyethylene. *L* is the length of the large period

conformation of a polymer chain in a crystal is characterized by the appearance of regularly repeating folds. In this case, the chain is said to have a fold conformation. For example, in a crystal whose thickness is 120 Å, a fold contains approximately 100 carbon atoms, while a molecule having a weight of 10^5 folds about 70 times.

The main parameter which quantitatively characterizes the lamellar structure is the fold length. As a fold is formed a chain may return to a crystal in various ways. Thus, the folding surface may have a regular structure if a chain, after coming out of a crystal, returns to it at a strictly definite distance (Fig. 5.8). However, even in this case, the crystal surface is defective owing to the stresses in places where a chain bends. The folding surface turns out to be quite disordered if a chain which comes out of a lamella returns to it not next to the place where it came out, but somewhat away from it or does not return to this crystal at all, forming long loops, free ends and other more or less defective regions (Fig. 5.8*d*). There may be various intermediate cases of the formation of folding surfaces in lamella (Fig. 5.8*b*, *c*). As a

result, the boundary regions must not be regarded as a part of a single-crystal. Therefore, a distinction must be made between the thickness of a crystal proper (which is usually known as a crystallite), i.e., region where the structure is the most similar to that of a single-crystal, and the magnitude of the large period or the folding period. The folding period is equal to the total thickness

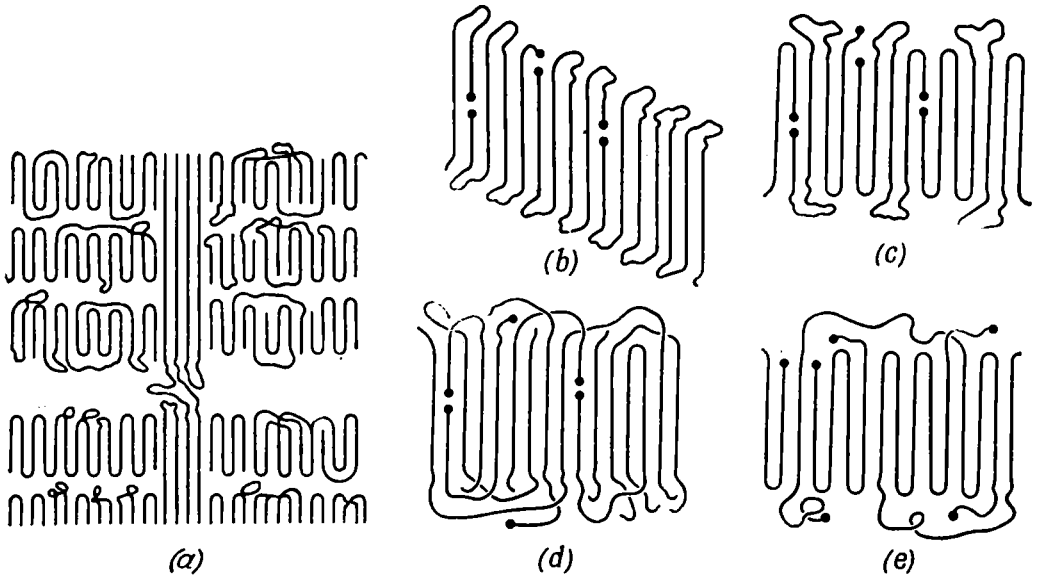


Fig. 5.8. Two-dimensional schematic illustration of folding surfaces in polymer crystals; *a-d* — possible cases of the arrangement of chains and their ends on folding surfaces

of a lamella, i.e., to the height of a crystallite plus the double thickness of the defective regions on folding surfaces.

The thickness of a lamella, the dimensions of a cristallite and the degree of defectness of the boundary layers of a single-crystal are decisively affected by crystallization conditions, especially by the degree of supercoiling ΔT, which is equal to the difference between the equilibrium melting temperature of a polymer and crystallization temperature.

When supercooling is about 15-20 °C or somewhat higher, crystallization causes the formation of crystals in which chains are in fold conformations.

Polymer crystallization under conditions which maximally approximate equilibrium ones at very low ΔT (up to 1 °C) results in the formation of very perfect single-crystals which are made of extended chains. Single-crystals with extended chains (this refers to crystals whose length along axis *c*, which coincides with the direction of macromolecular chains, is at least 2000 Å) are the most perfect forms of structure formation in polymers.

The simplest way of obtaining crystals with extended chains is crystallization under high hydrostatic pressure, which is usually of the order of $(5\text{-}10)\times 10^3$ atm. This raises the melting point of a polymer T_{melt} and accelerates crystallization at a selected, very low degree of supercooling ΔT.

Crystals having extended chains are formed also in the course of prolonged (for several weeks) annealing of polymers near the

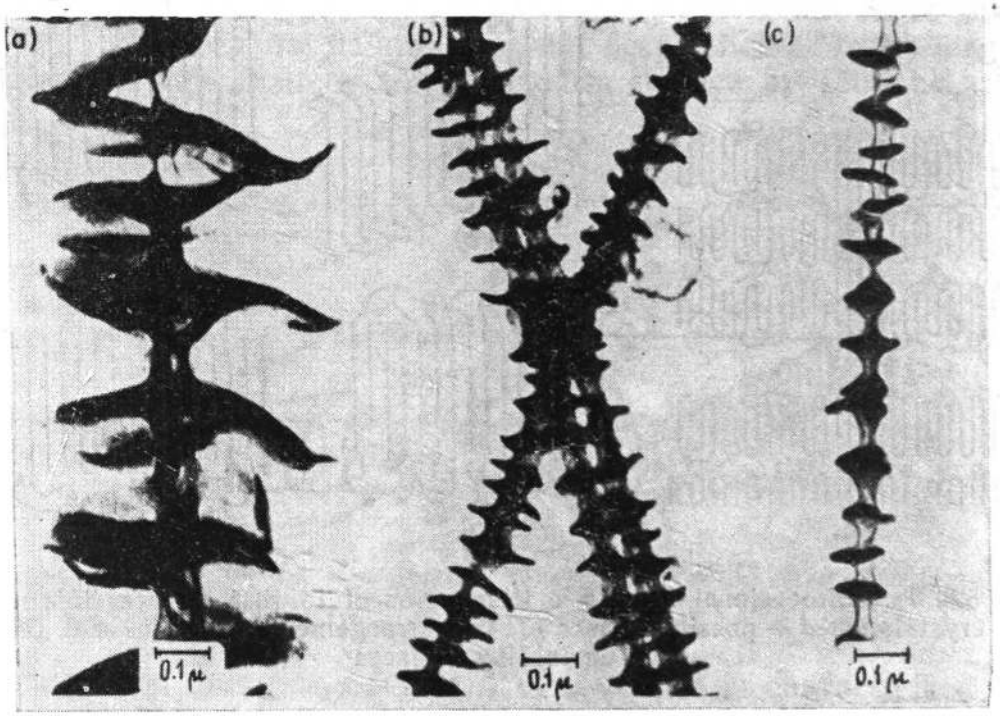


Fig. 5.9. Structural formations of the "shish-kebab" type in polyethylene (*a*, *c*) and a diagram of the arrangement of chains in them (*b*)

melting point or when a highly-oriented (extended by 1500 per cent) polymer, say polyethylene, is annealed under high pressure (about 7000 atm) in the range of temperatures which are similar to the equilibrium melting temperature T°_{melt} under given pressure.

Since crystallization under conditions which maximally approximate equilibrium ones causes an increase in the fold length, crystals having extended chains should be regarded as the equilibrium (thermodynamically advantageous) form. The formation of fold conformations of chains is due to kinetics.

The most important practical technique of obtaining crystals in which the chains retain their extended conformations to a considerable extent is crystallization with melt cooling under great deformations. The structural forms known as "shish-kebab", which originate in this case, are characterized by the presence of a long

fibrillar central trunk (see Fig. 5.9) that is formed by molecules of a high molecular mass mainly in an extended conformation. Laminae, whose chains are in fold conformations, grow transversally on this trunk, like on a nucleus. Similar structures are obtained also in the crystallization of some polymers from solutions with intensive stirring.

Structural formations which are obtained under diverse conditions of crystallization and are usually classified as single-crystals

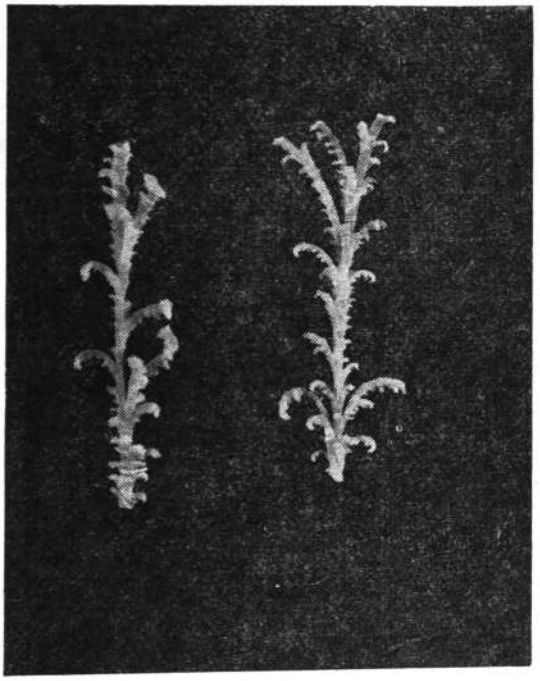


Fig. 5.10. Dendrite types of real polyethylene single-crystals

may be represented by a large number of regularly cut morphological forms, which as a rule have a lamellar structure and consist of many single lamellar formations. They include terrace-like crystals, single-crystals in the form of hollow pyramids of different shape, and dendrite formations, which are similar to those originating when metals crystallize into bars (Fig. 5.10).

Lamellas are primary structural elements, whose different arrangement causes a great diversity in the structural forms of crystal polymers. Thus, structure-formation on the basis of lamellar crystals develops further when the concentration of a solution from which they are obtained is raised or crystallization is carried out in relatively thin films (up to 30 μm). In such cases, crystalline structures characteristic only of polymers are formed as polyhedrons (they are known as hedrites and axialites) or ovals (ovoids),

an example of which is given in Fig. 5.11. Such structures have the appearance of single-crystals, but they have very large size: their length may reach several millimetres, while their thickness, 1 μm. In hedrites, macromolecular chains are perpendicular, while in ovoids, parallel to the base. These formations are compact structures formed by many (even more than 100) lamellas which are packed in a definite way and are united along the same crystallite

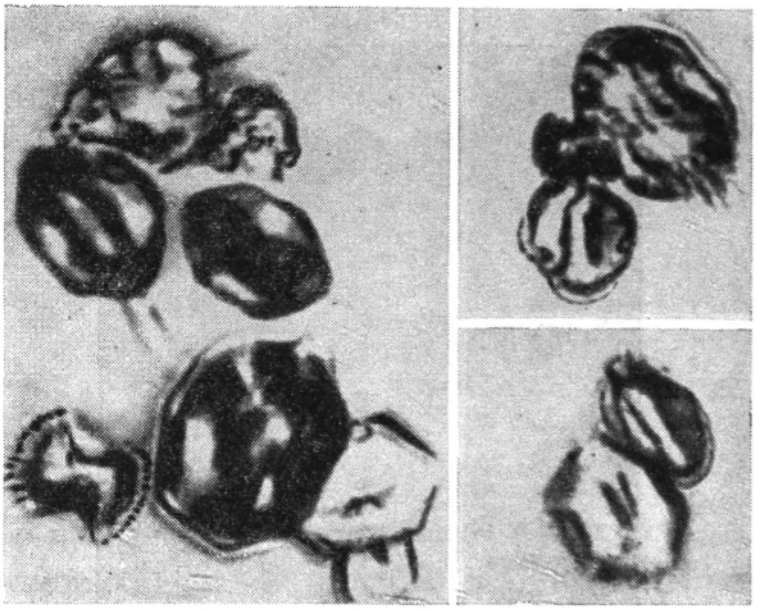


Fig. 5.11. Various types of polyethylene axialites

axis. Chain folds from real interfaces in such structures, but the lattice is oriented in the same way throughout the volume, as a result of which such structures are related to the single-crystal class.*

Formations of the type of hedrites and ovoids by their dimensions and degree of perfection hold an intermediate place between highly regular single-crystals and spherulites, which are higher structural forms in a crystallizing polymer.

5.2.4. Fibrillar Crystals

Fibrillar crystals having the appearance of ribbons are formed under conditions which hinder the formation of lamellar single-crystals (at high rates of evaporation of a solvent from a modera-

* A detailed description of the morphological forms considered above and their structural features can be found in the monograph *Polymer Single-Crystals* by H. Geil. Interscience Publishers, N. Y.-London-Sidney, 1963.

tely concentrated solution or at cooling of the melt). Fibrillar crystals usually have a thickness of 100-200 Å, while their length reaches many microns. Some authors believe that fibrillar crystals are formed by the aggregation of rolled lamellae. Others hold that lamellae degenerate in the formation of a fibrillar crystal, and therefore the crystal grows mainly in one crystallographic direction. Molecular chains in such fibrillar crystals are perpendicular to the longer crystal axis and have a fold conformation.

Fibrillar crystals are obtained also in crystallization carried out directly in the course of stereospecific polymerization. The formation of some structures or others in this case is determined by the ratio of the rates of growth of a chain and its crystallization, and therefore crystals made of either extended or folded chains are obtained by changing this ratio.

5.2.5. Globular Crystals

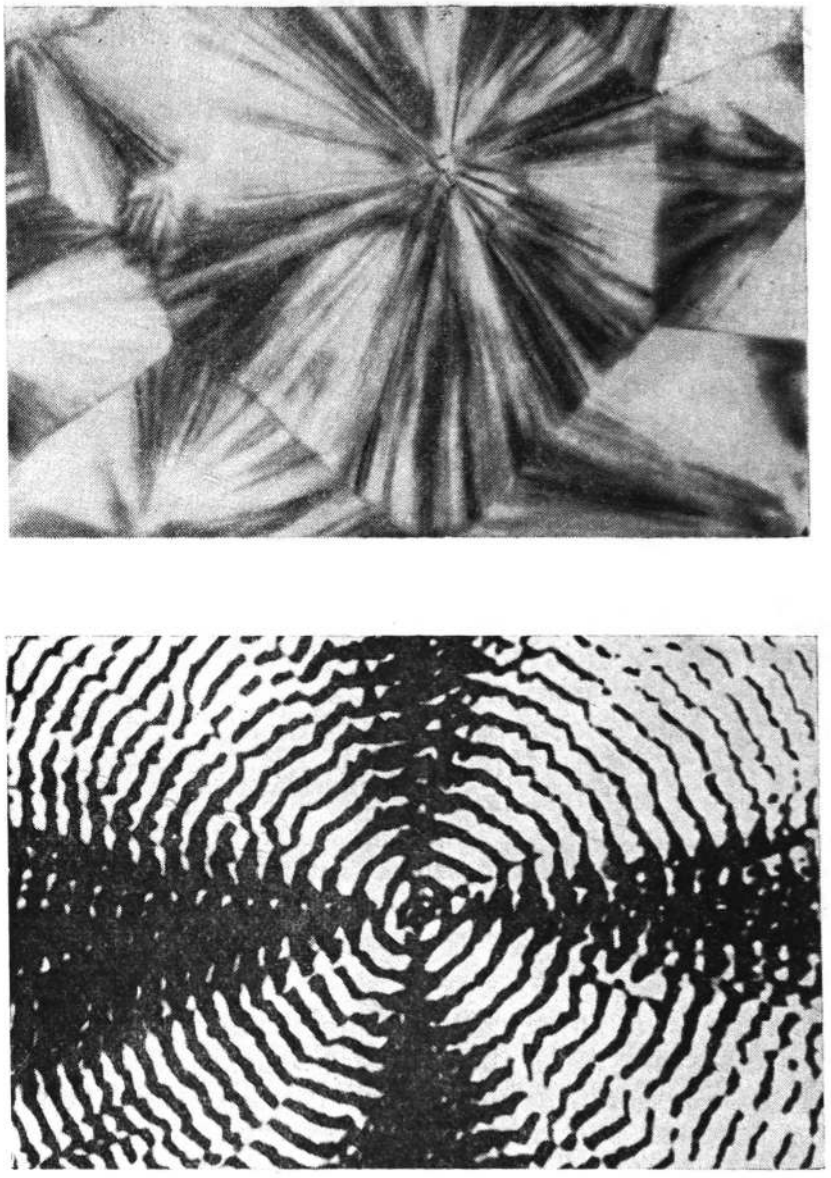
In such crystals, lattice points are formed by individual macromolecules in coiled (or globular) conformations, while the mutual arrangement of globules in space is quite regular, like in any single-crystal. The formation of globular crystals is characteristic for biopolymers, because a prerequisite of the formation of such a structure is a very high degree of uniformity of macromolecules by their dimensions, and this is attained almost exclusively in biological polymers. The best example of such crystals is the single-crystal of the tobacco mosaic virus. Such single-crystals have not been obtained for synthetic polymers.

5.2.6. Spherulites

A spherulite is a spherically symmetrical formation made of radial rays diverging from the centre. Spherulites grow in crystallization under the conditions of high viscosity or great supersaturation of a medium, i.e., when polymers crystallize from melts or concentrated solutions. The dimensions of spherulites range from several microns to fractions of a millimetre, reaching values of a centimetre in some cases.

Spherulites are made of crystalline fibrillar or lamellar structural elements (crystallites), which grow radially from one common centre. Macromolecular chains in a spherulite are arranged perpendicular to the radius or, in any case, they form an angle with it that is at least 60°, i.e., they are arranged tangentially to the spherulite radius.

Spherulites are typical crystalline formations, which are obtained under the real conditions of production of various polymeric articles, such as casts, films and fibres, for practically all the classes of crystallizing high-molecular compounds.



(a)

(b)

Fig. 5.12. Radial (*a*) and ring (*b*) spherulites of polymers

Spherulites are seen (discerned) best of all when thin films or cuts of polymers are examined in an optical microscope in polarized light. Spherulites possess anisotropic properties owing to the radial symmetry of their structure. Therefore, the indices of the refraction of light in radial and tangential directions are different, and birefringence characteristic of spherulites is seen in polarized light (Fig. 5.12). This birefringence is observed, because the orientation of crystallographic axes continuously changes in a spherulite along the angular coordinate. This corresponds to the same

continuous change of the refractive indices with respect to the plane of polarization of incident light. Therefore, various regions of a spherulite transmit polarized light differently. This results in appearance of a light-coloured circular birefringence region intersected by a dark figure in the form of a Maltese cross, whose arms are parallel to the directions of extinction of incident light (Fig. 5.12*a*). If the value of the index of refraction measured in the radial direction is greater than that in the tangential one, such a spherulite is called *positive*; otherwise, it is called a *negative spherulite*.

The orientation of structural elements along the spherulite radius intermittently changes rather often. A system of alternating dark and light rings is then superimposed on the picture of the Maltese cross (Fig. 5.12*b*). A distinction is made between *radial* or *ring* spherulites, depending on whether the figure of the Maltese cross or the system of circumferences dominates the picture observed.

In radial-type spherulites, one of the axes of the crystalline lattice retains a constant direction along all the radial directions.

Ring-type spherulites are built of lamellar crystals, whose orientation continuously changes along the spherulite radius. Therefore, the directions of crystallographic axes gradually twist with respect to the radius, forming right-hand or left-hand helixes. Orientation changes in every radial direction, and this is exhibited in the origination of alternating dark and bright rings.

The same polymer may form spherulites of different types, depending on crystallization conditions, and therefore the dominating form of crystallization in every specific case is connected with the degree of supercooling, which determines the kinetics and morphological features of crystallization. Ring-type spherulites are usually formed at low degrees of supercooling, and radial spherulites mainly grow at high ones. By changing the temperature in the course of crystallization, regions typical of both structural forms, the so-called "mixed" spherulites, an example of which is given for polypropylene in Fig. 5.13, can be obtained within the limits of even a single spherulite.

The formation of spherulite structures passes through several stages. The first two stages are the formation of crystal nuclei, which are statistically scattered throughout the volume of the sample, and the radial growth of independent discrete fibrillar or lamellar crystalline structures (primary crystallization), which occurs at the same rate in all directions. Then, encountering one another, spherulites continue to grow into regions which are still not crystallized, filling the entire volume of a body. Thus, their boundaries are distorted and a spherulite assumes the form of a polyhedron, and not of a sphere. After the radial growth of spheru-

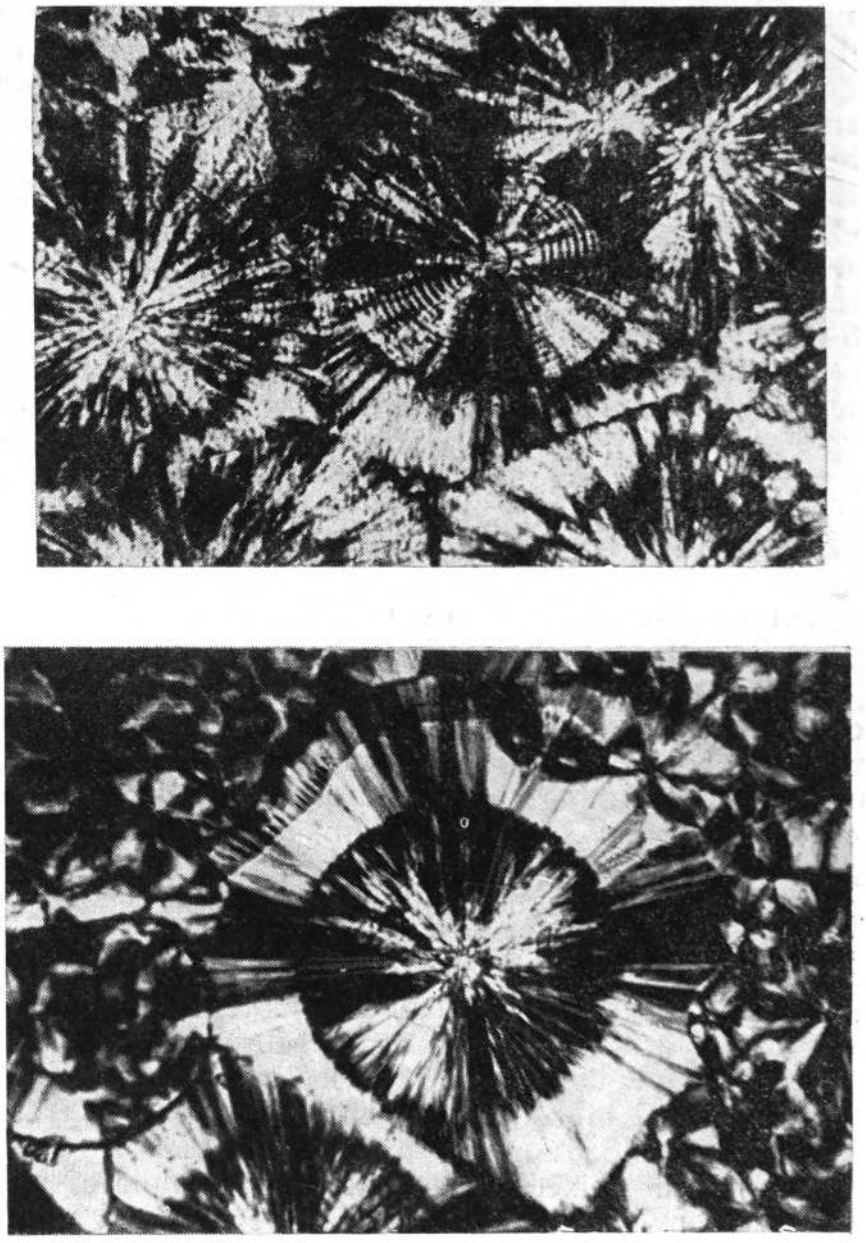
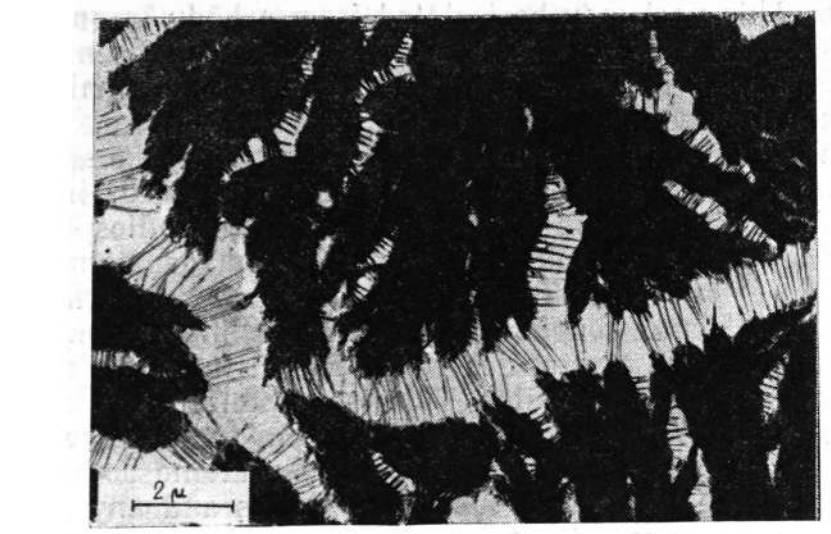


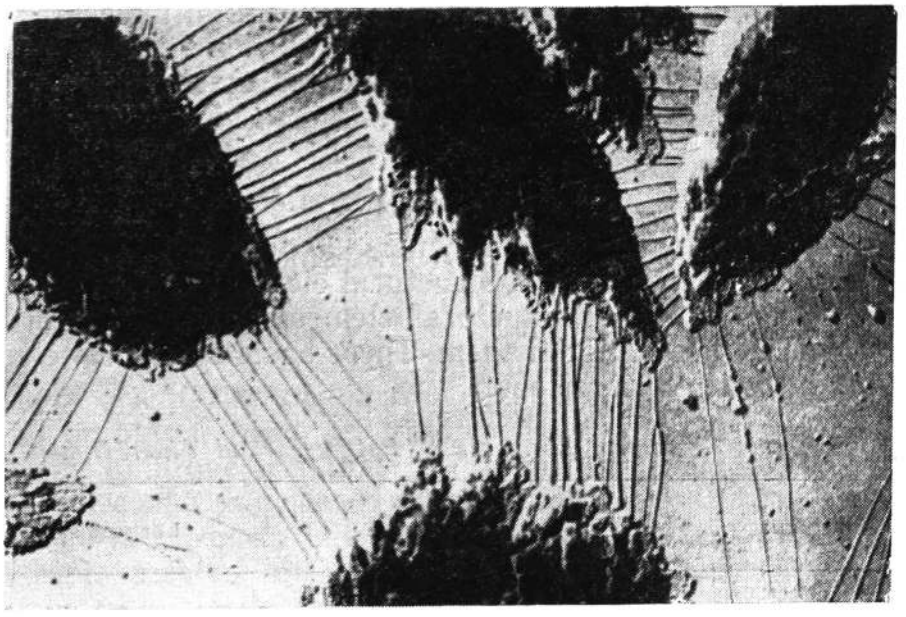
Fig. 5.13. "Mixed" spherulites of polypropylene

lites is completed, the final stage of crystallization (so-called secondary crystallization) begins, and during it the spherulite structure becomes more perfect and the melt, which has hitherto remained uncrystallized between the structural elements of a spherulite, crystallizes further.

Thus, spherulites are complex polycrystalline formations composed of the simplest structural forms. Such a spherulite structure is inevitably connected with the growth of the extent of defective-



(a)



(b)

Fig. 5.14. Interstructural bonds with a spherulite structure of polyethylene: *a* — between fibrils within the limits of a single spherulite; *b* — between various spherulites

ness of a crystalline structure in comparison with that which originates in the simplest structural elements. In addition, spherulites naturally have all the defects characteristic of the simplest structural forms: local distortions of crystalline lattices, unordered surfaces of folding of macromolecular chains, and so forth. Moreover, even when the crystallization is completed a part of material of a spherulite may remain amorphous and not enter into crystalline

formations. This part may be isolated from a body in one way or another (e.g., by eching a polymer), and it thus represents a truly amorphous phase. Macromolecules in such regions mainly have the form of globules.

The simplest structural elements in a spherulite, like spherulites themselves, are interconnected by a large number of interstructural bonds in the form of *tie macromolecules*, bundles of macromolecules or crystallized fibrillar formations made mainly out of chains in an extended conformation. Such bonds are formed if several macromolecules begin to crystallize simultaneously from both ends in various crystallites which are in the same spherulite or even in different spherulites. This is possible owing to a very weak correlation of the motions of the chain segments which are very far away. Such interstructural bonds combine both separate crystallites inside lamellae or fibrillar crystals and any other elements of a polymer structure. An example of interstructural bonds is given in Fig. 5.14. Their formation is specific for polymers and becomes possible only when a certain, rather high molecular mass is attained. For example, as regards polyethylene, such bonds are formed only in a polymer whose molecular mass is higher than 27 000.

5.2.7. Conclusion

At present, for crystalline polymers, a distinction is made between the definite sequence of structural elements according to the increasing complexity of structural elements and to the order of dimensions characteristic for them. These basic structural elements are given in the following table:

TABLE 5.1. *Basic Structural Elements of Polymers and Their Dimensions*

Element	Smallest size, Å	Largest size, Å
Molecule	2-5	10^3-10^5
Crystalline cell	3-5	25-30
Crystallite	20-100	100-500
Fibrillar crystal	up to 100	10^4-10^5
Single-crystal	100	10^3-10^4
Hedrites, ovoids	10^2-10^4	10^4-10^6
Spherulites	10^5-10^7	more than 10^7

As the dimensions of structural elements increase, the differences between their smallest and largest dimensions disappear, the individuality of macromolecules gradually levels out, and the cha-

racter (degree) of supermolecular order becomes more determinative in the exhibition of various polymer properties. The formation of complex supermolecular structures from the simplest elements is not a simple "putting together of blocks" into complex structures. The real process of formation of complex supermolecular crystalline structures and, accordingly, their disintegration caused by heating or mechanical effects is stepwise in the sense that complex elements are always made out of the simplest elements. But any structural elements up to a single molecule can participate in the elementary act of the formation of complex supermolecular structures. Thus, a complete description and deciphering of a crystalline polymer structure consists in the determination of: conformations of macromolecular chains in a crystal; the type and parameters of an elementary crystalline cell; the dimensions of crystallites and amorphous regions; the basic morphological structural formations in a polymeric body (plates, fibrils, globules, spherulites, etc.), and the arrangement of the simplest structural elements in complex ones (e.g., the arrangement of macromolecules in lamellae, single-crystals and the subsequent distribution of these elements in hedrites, spherulites, etc.). All this constitutes the subject of the study of structure-formation in polymers.

5.3. ORIENTED STATE OF POLYMERS

An extremely great anisotropy of the dimensions of macromolecules, which is a principal feature of the structure of polymeric bodies, makes it possible for the oriented state, which is just as specific for polymers, to exist. It is characterized by the great prevalence of orientation of macromolecules in one (uniaxial) or two (biaxial or planar orientation) directions, and this results in the anisotropy of properties that is just as strongly pronounced. An extreme case of the oriented state would be the parallel packing of all macromolecules, but, in almost all the real cases, such a structure is created only on the average, because flexible-chain macromolecules partly retain fold conformations characteristic of the isotropic state of polymers. In an oriented state the difference between amorphous and crystalline polymers vanishes, as a result of which it should be regarded as an independent state of a polymeric substance.

The main features of the oriented state of polymers are the above-mentioned preferential orientation of macromolecules along the direction of extension, the fibrillar structure of a body with the arrangement of chains along the fibril axis (contrary to the transverse arrangement of macromolecules relative to the axis of a fibril in spherulites and fibrillar crystals, as we have seen earlier), and the presence of a large period along the fibril axis

which corresponds to the alternation of more ordered (crystalline) regions and amorphous layers.

The structure of polymers in an uniaxially oriented state is represented most clearly by Peterlin's model (see Fig. 5.15). The main features of this model are: a clear division of the structure into microfibrils (in the figure, they are divided by a dotted line)

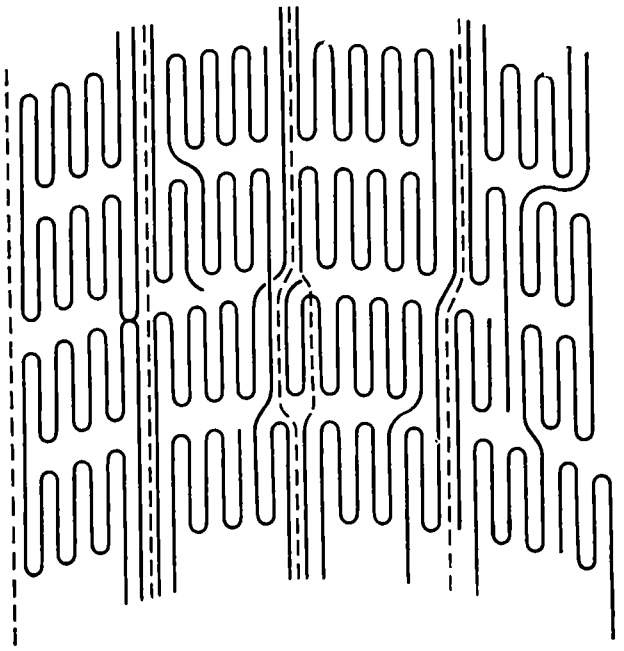


Fig. 5.15. Peterlin model of the structure of oriented polymers

having a diameter of 100-200 Å; transversal alternation of crystalline blocks, in which chains retain fold conformations, which are divided by defective (less ordered) layers, and the presence of a large number of intra- and a considerably smaller number of interfibrillar tie chains. Microfibrils combine into larger fibrils having the size of the order of 1000 Å, which create the macrostructure of oriented bodies that is observed.

The most important feature of this model is the presence of tie chains. The existence of a small number of interfibrillar tie chains clearly explains the low binding of microfibrils. As a result, uniaxially oriented articles have very low transverse strength and are readily split into separate fibrils. Oriented articles are characterized by considerably higher values of strength and elasticity modulus, and by lower deformability in comparison with an isotropic body. This is easily explained by both the preferred orientation of macromolecules and a decrease in their conformation set. But all these mechanical characteristics are considerably lower

than the theoretically calculated ones for a completely oriented and homogeneous body. It is also evident from Peterlin's model, which shows that when microfibrils are extended, the entire load falls on tie chains, and a body is destroyed (ruptured) as a result of the rupture of tie chains. The share of tie chains (those working under stress) is small in weak sections, because the bulk of the chains (even in an oriented state) is in a fold conformation.

Peterlin's model applies mainly to flexible-chain polymers. The necessary presence of folds in their structure makes the ultimate (theoretical) strength of a material unattainable. The possibility of approximation to maximum values of strength is connected with the production of oriented articles out of rigid-chain polymers, which cannot form folds and therefore produce a structure where all the chains are packed almost parallel.

The oriented state of polymers is of fundamental importance to such articles as fibres and films. In the first case, a uniaxially oriented state is created, and, in the second, the character of orientation may change from a strictly uniaxial to a planar orientation, depending on the purpose of a film.

5.4. STRUCTURE OF AMORPHOUS POLYMERS

We have seen that polymeric substances are characterized by a continuous transition, according to degree of ordering, from an ideal order, a single-crystal, to an absolutely disordered state, and the estimate of the degree of ordering may be different, depending on the level of the dimensions on which observations are made. An estimate based on X-ray method is the most common one. Experiments have shown that reflexes which correspond to the existence of a crystalline lattice are not observed for very many polymeric systems. Such a situation exists, in particular, for polymers which, for one reason or another (irregular structure along the chain, high rigidity of a macromolecule, steric hindrances, etc.), cannot in principle crystallize. The crystalline order is also absent in melts and solutions of polymers where the crystalline lattice is destroyed by thermal motion. Moreover, a nonequilibrium structure which corresponds to the state of a melt can be preserved (fixed, frozen) in various crystallizing polymers by rapid cooling. In the last case, both a completely amorphous polymer and a body where crystalline and amorphous regions coexist can be obtained. All the above-mentioned cases form a group of noncrystalline bodies which are sometimes incorrectly called amorphous polymers.

The incorrectness of using the term "amorphous" with respect to noncrystalline polymers is connected with the existence of a definite degree of structural ordering in them. This idea was first

expressed by V. A. Kargin, G. L. Slonimsky and A. I. Kitaigorodsky, who proposed the so-called "bundle" (cluster) model of the structure of noncrystalline polymers. The main element in this model was a "bundle", i.e., a set of macromolecules which are packed almost parallel and have large longitudinal dimensions. The ideas expressed by Kargin and his school on the existence of a definite degree of ordering within the limits of a non-crystalline state are of fundamental importance in understanding the structure and properties of amorphous polymers (both solid polymers,

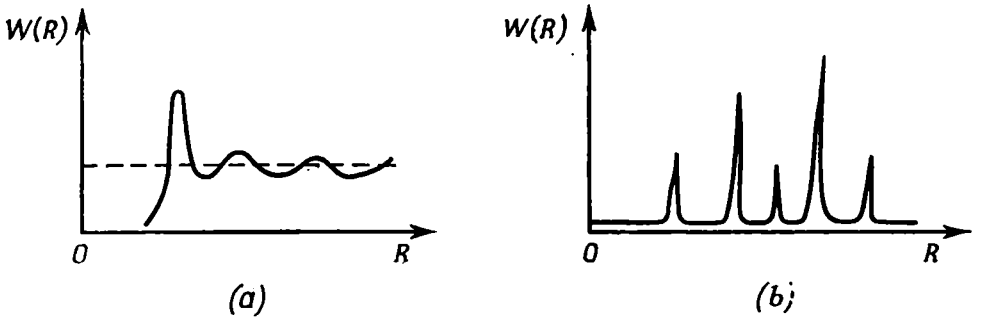


Fig. 5.16. Appearance of the function $W(R)$ for (*a*) an amorphous substance and (*b*) a crystalline substance

and melts and solutions), and they have been fruitful in the development of subsequent investigations.

The structure of amorphous polymers is quantitatively described by means of the function of radial distribution of interatomic distances $W(R)$, which represents the relative probability W of finding neighbouring atoms at distance R from a certain fixed atom. For a crystalline substance, this function is shown in Fig. 5.16*b*, which shows constant distances (equal to the periods of a crystallographic cell) at which neighbouring atoms are arranged. This picture reflects the existence of a long-range order in a body. It considerably changes for non-crystalline polymers. The function of the radial distribution for them is shown in Fig. 5.16*a*. We can see that the function of interatomic distances $W(R)$ becomes continuous; it includes several attenuating oscillations relative to unity. The maxima of this function correspond to more probable intermolecular distances, while the minima, to distances at which neighbouring atoms are encountered relatively rarely. The first high maximum conforms to the fact that the probability of an ordered arrangement of the first particle layer relative to the fixed particle is very great, i.e., there is a short-range order in the arrangement of macromolecules in amorphous polymers. Such an order exists in any liquid and is connected with density fluctuations, which result in ordered clusters or associates.

As Fig. 5.16*a* shows, the height of the subsequent maxima of the distribution function sharply diminishes, and therefore the probability of finding the atoms of neighbouring molecules at any distance from the selected centre becomes the same, $W(R) \to 1$. This corresponds to the absence of a long-range order in an amorphous substance and to the appearance of an amorphous halo on the X-ray patterns of amorphous polymers.

The position of the first, most intense amorphous halo on the X-ray patterns of most non-crystalline polymers conforms to angles θ, which correspond to distance d between scattering centres that is equal to 4.5-5 Å, while that of the second, less intensive halo, to approximately 10 Å. The presence of these maxima is connected with the fact that macromolecules or segments of macromolecules are packed in a definite order, being almost parallel to one another.

In the case of various effects on a polymer (annealing, mechanical load, irradiation, etc.), these maxima may somewhat change their place and intensity. This shows the effect of the given factors on the structure of non-crystalline polymers and, in turn, it causes a change in their physico-mechanical properties.

Thus, the main feature of non-crystalline polymers is the short-range order, characterized by a size of up to 10 Å, at absence of a long-range order. But the development of ordering in them is not confined to this. Higher levels of structural organization are detected by means of dark-field electron microscopy. This method makes it possible to isolate regions on the electron-microscope image of an object that correspond only to definite Bragg's reflexes. In this case, the entire useful field turns out to be dark and only the ordered region where the scattering of the electron flow produces a selected Bragg's reflex is examined. The employment of this method has shown that, like in crystalline polymers, where folding chains form a crystalline lamella, amorphous polymers have its remote analogue, i.e., a "domain" of the order of 30-100 Å. A short-range order is observed within such a domain, being expressed in the parallel arrangement of chains, which assume a fold conformation. Therefore, owing to chain folding, parts of macromolecules in the domain are arranged parallel to one another, like in a lamellar crystal. But defectness (i.e., deviation from a crystallographic order) is very great in the domain. It is assumed that domains are connected with one another by tie chains, like beads in a necklace. Such domains cannot be regarded as truly amorphous regions; they are a transitional type of structure, the transition being from an amorphous to a crystalline state of a substance. In addition to them, a non-crystalline polymer has truly amorphous regions, which are formed mainly by chain ends,

parts of macromolecules which belong to tie chains, macromolecules of a low mass, and so forth.

As a result of the detection of the three basic components of a non-crystalline polymer structure (domains, tie chains and truly amorphous regions), Yeh built a model of the structure of an amorphous polymer, which is shown in Fig. 5.17.

Besides direct structural investigations, there are three groups of indirect considerations which are the basis for conclusions on the ordering of non-crystalline polymers.

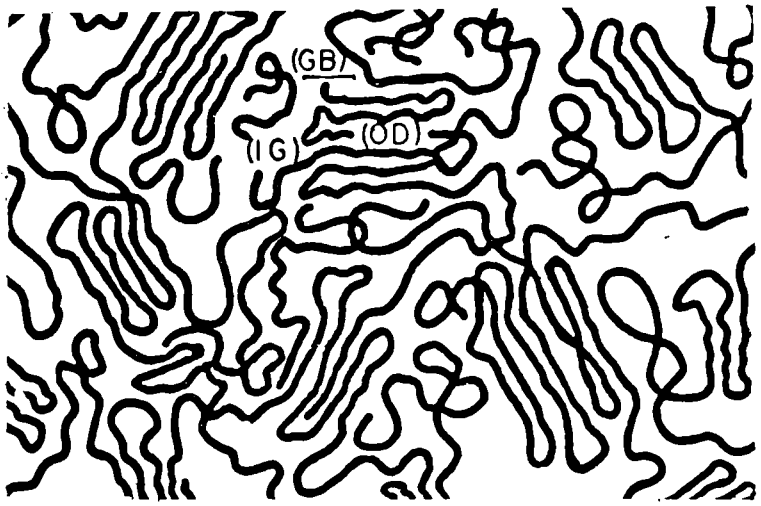


Fig. 5.17. Model of a polymer melt structure according to Yeh: *OD* – ordered domain; *GB* — grain boundaries; *IG* — intergranular region

The first one of them is based on the similarity of the values of the density of amorphous and crystalline polymers. For example, the density of ideal crystalline polyethylene is 1.00, while that of amorphous polyethylene is 0.8 g/cm^3. This indicates that the difference in the packing of macromolecules in both states is not too great. Indeed, direct calculations show that if chains in a non-crystalline polymer assume statistically the most probable conformations, like say in maximally dilute solutions, the densities of amorphous polymers would be far lower than their real values owing to steric and energetic hindrances when the chains are packed.

The second one is connected with kinetic data. Very high rates of crystallization of crystallizable polymers cannot be understood if it is believed that a transition is made from a completely amorphous state, where chains are randomly (statistically) entangled with one another, to an ordered structure. The motion of chain segments as macromolecules are "disentangled" and their diffusion in an extremely viscous melt in adjustment to the lattice

being formed requires much more time than the really observed times of crystallization. The high rate of crystallization can be explained only if account is taken of the fact that ordered regions already exist in a melt. It turns out that small segmental motions are enough for their crystallization. The above-mentioned domains which were detected in amorphous polymers may be such crystal nuclei. In this case, crystallization is effected in a way that a domain directly forms a crystalline lamella and on its surface chains fold further. It is also out of these considerations that the residues of a structure which existed in a crystalline polymer below the melting point are preserved for a long time in a melt. As a result, "structural memory" is observed, being expressed in the fact that, when crystallization is repeated, crystallites grow in exactly the same places where they existed before melting. These experiments show that a high degree of structural ordering is preserved in a melt.

Lastly, the third group of indirect considerations consists of numerous measurements of the mechanical, electric and other properties of non-crystalline polymers. The results of these measurements show that the properties of non-crystalline polymers greatly depend on their prehistory (thermal and mechanical prehistory, the prehistory of dissolution in solvents of a different thermodynamic quality, etc.), because the amorphous state is a nonequilibrium one and various structural forms having different properties may be registered within its limits, as is the case with crystalline polymers having different morphologies. This also determines the change in the properties of non-crystalline polymers with time, particularly in annealing. In this case, a transition is gradually made to structural forms of higher equilibrium, being reflected on the macroscopic properties (limiting, relaxational, etc.) of a body that are being measured. Measurements of the characteristics of macroscopic properties of non-crystalline polymers also show that not only elements whose size is tens of angstroms, but also considerably larger structural formations should be preserved in their structure. This is evident from the very strong effect of some microadditives on the properties of non-crystalline polymers. The effectiveness of the action of low-molecular additives introduced into a polymer in an amount reaching several fractions of a per cent may be explained by their influence on the relative displacement of structural elements only if the value of the latter approximates a micron. The amount of the additives introduced then turns out to be enough for their being distributed over the surface of such structural elements. Such considerations indicate the possibility of aggregation of domains into larger structural formations in the same way as spherulites grow from lamellar and fibrillar crystals in crystalline polymers. Proceeding

from this assumption, V. A. Kabanov et al. proposed a new model of amorphous polymers where the formation of a "superdomain" structure of a substance is postulated.

Thus, direct proof and indirect considerations show that amorphous (non-crystalline) polymers are bodies which have a definite degree of structural ordering. This brings many of their structural features and physico-mechanical properties closer to similar characteristics of crystalline polymers and results in the effect of the supermolecular structure of amorphous polymers on their properties to be exhibited in various ways.

5.5. SUPERDOMAIN STRUCTURE IN AMORPHOUS POLYMERS

A specific and practically important case of the formation of a highly ordered structure within the limits of the amorphous state of polymers is the formation of a highly ordered superdomain structure in block-copolymers. Let us consider this phenomenon by taking an example which is the most characteristic of block-copolymers, the A-B-A structure, where B is the polybutadiene (or polyisoprene) block, while A is the polystyrene block. An important fact is that, in such block-copolymers, block lengths are constant with a rather high degree of accuracy, and blocks of the same type are segregated into a domain. The distance between domains of the same type is determined by the length of blocks of a different structure. The distance between blocks of type B is strictly constant owing to the constancy of the length of blocks of type A, and therefore the domains which consist of segregated blocks B form a quasicrystalline superlattice having a characteristic period of the order of 1 μm. Such a structure is very similar to the structure of globular crystals, where it also originates owing to a high degree of uniformity of the masses of macromolecules.

The ordered superdomain structure described for block-copolymers is characteristic of microheterogeneous amorphous polymers and is determinative in the exhibition of the physico-mechanical properties of these bodies.

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CHAPTER 6

Phase States and Phase Transitions of Polymers

For an understanding of many of the technological and physicochemical processes occurring in polymeric materials it is very important to get an insight into present-day views on the phase states of polymers. These views are based, firstly, on the general ideas of phase states, developed for low-molecular substances and, secondly, on the experimental data on polymer structure discussed in the previous chapter. It will be useful to start with a general consideration of the concepts of phase, phase states, phase transitions, and the properties of substances in different phase states.

6.1. GENERAL CONCEPTS OF PHASE STATES AND PHASE TRANSITIONS

6.1.1. State of Aggregation and Phase State of Matter

One distinguishes between the state of aggregation and phase state of matter. Substances can exist in three aggregation states — gas, liquid, and solid. These states differ in the kind of motion and in the packing of the molecules or atoms.

Molecules in the *gaseous* state possess translational, rotational, and vibrational motions. At temperatures much higher than the critical, the distances between molecules in a gas are fairly large, i.e., its molecules are loosely packed.

In the *solid* state the distances between the molecules are small (close packing). The molecules have practically no translational or rotational motion, but vibrate about fixed centres of equilibrium at a frequency of the order of 10^{13}-10^{14} vibrations per second. Low mobility of the molecules or atoms accounts for the resistance of solids to changes in shape, i.e., their solidity.

The *liquid* state is intermediate between the gaseous and solid states. Liquids approach gases in molecular motion and solids in packing density. Possessing considerable mobility, the molecules of a liquid move readily, and their centres of equilibrium are continually changing their positions. That is why liquids change their shape readily and flow under the influence of small stresses.

The difference in mobility of molecules stipulates different mechanisms of diffusion in the liquid and solid states. In the liquid and gaseous states diffusion occurs by what is known as a group mechanism, consisting in the molecules moving jointly with adjacent molecules which can simultaneously move apart and make place for other molecules. In solids, diffusion occurs only by elementary skipping of atoms to neighbouring unoccupied sites which are always present in the body owing to the imperfection of structure of real crystals. That is why diffusion in solids is much slower than in liquids and gases. Evaporation of substances changes the coefficient of diffusion very little, but melting increases it by hundreds of thousands of times.

Molecular packing is approximately the same in the liquid and solid states, but is much different in gases (under ordinary conditions). When a crystalline substance melts, its density changes only a few per cent, but on condensation of vapours it increases by thousands of times. Close molecular packing is the main feature approaching a liquid to a solid, and distinguishing it sharply from a gas. Owing to close packing liquids are characterized by strong intermolecular interaction.

To get a clear idea of the *phase state* of matter it is necessary to consider the *phase* concept. The term phase can be defined structurally and thermodynamically (for low-molecular substances these definitions coincide). In thermodynamics, a phase is defined as part of a system separated from other parts by interfaces and differing from them in thermodynamical properties. A phase must possess sufficient extent (volume) for the concepts of pressure, temperature and other thermodynamic properties of the phase to make sense. Phases should be separable from one another. From the structural standpoint phases differ in the order of mutual arrangement of their molecules. Depending on this order one distinguishes between three phase states, namely: crystalline, liquid, and gaseous.

The *crystalline phase state* is characterized by a three-dimensional long-range order in arrangement of atoms or molecules. *Long-range order* is an order observed over distances hundreds and thousands of times greater than the size of the molecules, and may exist in one, two, or three dimensions. Long-range order in one dimension is that of an ideal molecular chain of a polymer in which the same unit is repeated regularly. Crystals are structures

having long-range order in three dimensions (ideal crystalline lattice).

The *liquid phase state* is characterized by absence of a crystalline lattice and it is often called *amorphous*. In this state the packing of molecules or atoms is approximately the same as in the crystalline state. Since the molecules or atoms are adjacent to one another, random arrangement is impossible. The amorphous state has *short-range order*, i.e., an order which is observed over distances commensurable with molecular size. In the vicinity of any given molecule its neighbours may be in a definite order, but at a small distance from the molecule this order no longer exists.

Short-range order in liquids can be detected by X-ray studies (Chap. 5) and is manifested as density fluctuations (deviations of density from the average value) and in the formation of ordered "cybotactic groups" or "clusters" of molecules, called associates.

For a long time the data of X-ray diffraction studies of simple liquids, which revealed the presence of ordered formations in them, were thought to indicate quasicrystalline structure of liquids. Nowadays these ideas are losing popularity. The tendency at present is to draw an analogy between liquid and gas, the more so that short-range order in molecular arrangement has been detected by X-ray diffraction in gases too at near-critical temperatures.

The liquid phase is the state of substances at temperatures above their melting points and of all solid amorphous substances (e.g., ordinary silicate glass, rosin, etc.). Since silicate glass has no crystalline lattice, all solid amorphous bodies are said to be *glassy* or *glasses*. Glassy and crystalline bodies are both in the solid aggregation state and do not differ in mobility and packing of their molecules.

It follows from the above discussion that the gaseous aggregation and phase states practically coincide. Two phase states may correspond to the solid physical state, namely, crystalline and amorphous (glassy). The liquid phase state covers two aggregation states: solid (glassy) and liquid (above the melting point).

6.1.2. Phase Transitions

Phase transitions are transitions from one phase to another, i.e., transitions involving a change in mutual arrangement of molecules and in thermodynamic properties of the substance.

Phase transitions may be of the first and the second order.

First-order phase transitions are accompanied by a discontinuous change of internal energy and specific volume. These transitions involve absorption or generation of heat (heat of transition); they include melting, vaporization, sublimation, and many transformations from one crystalline modification to another. At equilibrium

the molar and specific thermodynamic potentials of the phases are equal; hence, during a first-order transition the thermodynamic potential varies continuously, but its derivatives $(\partial G/\partial p)_T = V$ and $(\partial G/\partial T)_p = -S$ undergo a jump. The entropy jump ΔS equals the heat of transition divided by the absolute temperature $\Delta H/T$.

Phase transitions of the second order are transitions in which the internal energy and specific volume change smoothly; no heat is evolved or absorbed, but the first derivatives of internal energy and volume, i.e., the heat capacity $(\partial H/\partial T)_V$ and the compressibility $(\partial V/\partial p)_T$ change jumpwise at the point of transition. In other words, at a second-order transition point not only the thermodynamic potentials are continuous, but their first derivatives $(\partial G/\partial p)_T$ and $(\partial G/\partial T)_p$ as well; however, their second derivatives

$$\frac{\partial^2 G}{\partial p^2} = \left(\frac{\partial V}{\partial p}\right)_T; \quad \frac{\partial^2 G}{\partial p\,\partial T} = \left(\frac{\partial V}{\partial T}\right)_p; \quad \frac{\partial^2 G}{\partial T^2} = \frac{c_p}{T} \qquad (6.1)$$

show a jump.

Examples of such transitions are that of liquid helium (I) to liquid helium (II), many transformations in crystals, the transition of iron to the paramagnetic state at the Curie point.

6.1.3. Crystallization and Glass Transition

Since solids may exist in the crystalline or in the amorphous (glassy) states, there are inherently two possible ways of passing from the equilibrium liquid state into the solid state, namely, crystallization and glass transition.

Crystallization is the transition from a state of short-range order to one of long-range order, i.e., the process of formation of a new phase. It is therefore a phase transition of the first order.

Glass transition is the passage of a mobile liquid into the solid state with no change of phase, i.e., with retention of short-range order; hence, glass transition is not a phase transition.

Crystallization occurs at a strictly definite temperature (crystallization or melting point), below which the equilibrium state is the crystalline state, because the thermodynamic potential of the crystal is smaller than that of the liquid.

However, at temperatures below the crystallization point the same substance can be obtained in the liquid, or so-called *supercooled state*. A supercooled liquid is always in a *nonequilibrium state*, and sometimes insignificant changes in external conditions will cause crystallization.

When a liquid is cooled (and especially when it is supercooled), its coefficient of viscosity increases and its energy of thermal motion decreases ($E = kT$). This prevents the molecules from regrouping to form a crystalline lattice. At a certain temperature

the coefficient of viscosity of the liquid approaches 10^{13} poises, which corresponds to the viscosity coefficient of a solid. The supercooled liquid solidifies, but no crystalline lattice is formed, and the substance passes into the glassy state, i.e., becomes glassy or vitreous. The temperature at which the viscosity of the amorphous substance becomes equal to 10^{13} poises is called the *glass-transition temperature*, or *glass point* T_g. When a substance assumes a glassy state, all its properties change: it loses the properties characteristic of the liquid state and acquires the properties of a solid. These changes do not occur jumpwise, but gradually, over a certain temperature interval of about 10 or 20 °C. Therefore, the glass-transition temperature is not a point, but the average of this interval.

6.2. SPECIFIC FEATURES OF THE ORDERED STATE OF POLYMERS

Polymeric substances possess high molecular mass and hence their boiling points must be very high. Polymers decompose when heated (see Chap. 3), and their decomposition temperatures are always far below their boiling points. That is why polymeric substances cannot be converted to the gaseous state and exist only in the condensed state, liquid or solid. A study of the phase states and ordering of polymers reveals a number of specific features related to the large size of their molecules.

Let us examine theoretically the possibility of formation of an ordered structure in polymers. The concepts of short-range and long-range orders are defined by the ratio between the distance over which the order extends and the dimensions of the elements arranged in the order. In low-molecular substances these elements are molecules, atoms, or ions. A polymer has two types of structural elements: units and chains. Therefore in considering a short-range or long-range order it is necessary to indicate which of these elements the ordered state refers to.

Theoretically the existence of long-range order can be assumed in the arrangement of both chains and units. Long-range order of units in one dimension can exist in a long molecular chain of regular structure. The presence of such a long-range order is a prerequisite for crystallization of the polymer. However, this is a necessary but not a sufficient condition. For a crystalline polymer to form there must be long-range order not only in the arrangement of units, but of chains as well in three dimensions.

Figure 6.1 shows three possible degrees of ordering of long chains and units (after A. I. Kitaigorodsky).

Order of small structural elements (monomeric units) can be detected by electron diffraction techniques, and of long chains, by

means of the electron microscope. Comparison of electron diffraction and electron microscopic data for polymers shows that ordered formations of chains (*bundles*) can be observed in the absence of crystalline interferences on electron diffraction patterns (see Chap. 5). This is evidence that a high degree of ordering is possible in the absence of a crystalline lattice (see, for instance,

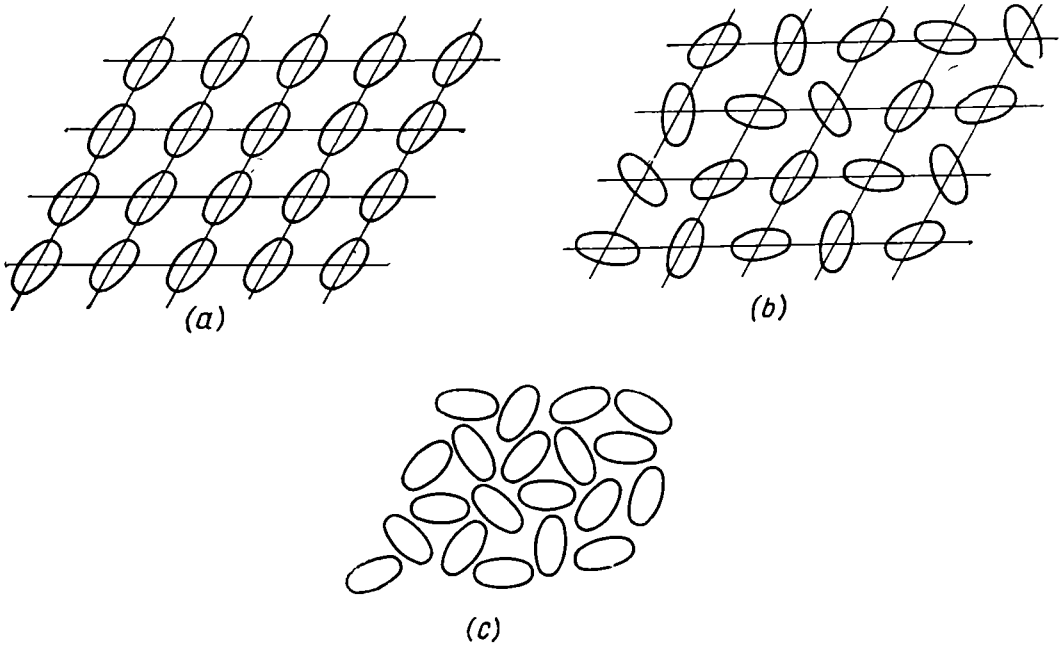


Fig. 6.1. Different modes of packing of chain molecules (ovals denote projection of monomeric unit of polymer chain):

a—long-range order of arrangement of both chains and units in three dimensions; *b*—ordered arrangement of centres of unit sections and unordered orientation of sections; chain axes form regular lattice; units are arranged disorderly; *c*—"liquid" arrangement of chain (long-range order of arrangement of units along each chain and short-range order of chain arrangement)

Fig. 6.1*b*). Crystalline polymer structure requires long-range three-dimensional order in both chain and unit arrangement (Fig. 6.1*a*). In this case the structure of the ordered sections can be characterized by unit cell parameters, just as in the case of low-molecular crystals.

It follows from this discussion that a high degree of ordering can be achieved in polymers in two ways: by crystallization or by chain orientation without orientation of monomeric units. These two kinds of ordering correspond to the two phase states of polymers, namely, crystalline and amorphous. In the crystalline state the long-range order in arrangement of chains and units is not necessarily very perfect, whereas in the amorphous state the short-range order in arrangement of chains may be very perfect. Such phenomena are observed in low-molecular substances too: for

example, very defective crystals and well-ordered liquids are known. However, a fairly perfect short-range order differs fundamentally from a fairly imperfect long-range order.

Crystallization of a polymer is a phase transition. Chain orientation not accompanied by orientation of units, i.e., the transition from state *c* in Fig. 6.1 to state *b* is not a phase transition, and the polymer remains amorphous.

6.3. CRYSTALLIZABILITY OF POLYMERS

In application to polymers one must distinguish between the concept "crystalline" and "crystallizable", because many polymers are incapable of crystallizing under any conditions. On cooling they solidify as the intensity of thermal motion of their units decreases, without forming a crystalline lattice, i.e., they become glassy.

A molten crystallizable polymer can be obtained in the glassy state by cooling it rapidly to a temperature much below its crystallization point. The glass temperature of such a polymer is naturally below its crystallization point ($T_g < T_{cryst}$).

Crystallizability of polymers is determined by their chemical constitution, depending on a number of factors also characteristic of low-molecular substances (packing, energy of intermolecular interaction and ratio of the latter to the energy of thermal motion), as well as on the specific features of polymer chain structure (chain regularity and flexibility).

Regularity of Polymer Chain. A crystal must have long-range order in three dimensions, one of which coincides with the axis of the polymer macromolecule. Hence, long-range order must exist in this direction, i.e., the chain itself must be of sufficiently regular structure. Sometimes even considerable irregularity in chains may be no obstacle to crystallization, but random copolymers and atactic polymers do not crystallize under any conditions.

Flexibility of Polymer Chain. Thermal motion affects crystallization in two ways: on the one hand, heating increases the rate of movement of the structural elements, favouring crystallization, but on the other hand, established order is disturbed and crystals break up. The thermal motion of large linear polymer molecules is negligibly small, and their crystallizability depends mainly on the thermal motion of their units, i.e., on their chain flexibility. Only polymers with sufficiently flexible chains can crystallize; rigid-chain polymers crystallize with difficulty.

In the temperature range where chain flexibility is too high, intense thermal motion disturbs orientation of the units and crystals cannot form. Therefore, to crystallize a polymer it has to be cooled to a temperature at which the motion of its units does not hinder their orientation, i.e., to the crystallization temperature.

However, excessive cooling of the polymer may lower the energy of thermal motion to such an extent that the units cannot rearrange themselves. This usually occurs below the glass-transition temperature of the polymer, where the thermal motion of the units is insignificant. Hence, crystallization of each polymer is possible only within a definite temperature interval, characteristic of that polymer, wherein its chain acquires *optimal flexibility*, namely, between the glass-transition and flow temperatures.

If the glass temperature of a polymer is much above room temperature, the polymer must be heated above its glass temperature before it can crystallize. For example, the glass temperature of isotactic polystyrene is about 100 °C. Below this temperature it will not crystallize. But above 100 °C it forms crystals which melt at 220 °C. For this reason single crystals of isotactic polystyrene are produced only from hot solutions.

Packing of Molecules. One of the most important principles of crystal chemistry is the principle of closest packing, according to which the most probable and hence the most stable structure is that to which corresponds close packing of the ions, atoms, or molecules in the crystal. This leaves the least free-space volume between the particles. Like low-molecular organic substances, polymers obey the principle of close packing, and macromolecules must be packed as closely as possible in the crystalline lattice. There are several possibilites for formation of close packings of polymer chains.

The first is a crystalline structure built by close packing of spheres. Such crystalline formations are observed in so-called globular proteins, the globules of which remain stable even when they come in direct contact with each other. The possibility of formation of a crystalline structure under such conditions is due to the spheres being all equal in size, which is related to the monomolecularity of natural macromolecular compounds.

The second possibility of close packing is the packing of helical macromolecules. In this case the convexities of one helix fit into the concavities of another.

And finally, the third possibility is packing of long extended chains, characteristic of polyamides, polyurethanes, etc. Here the important factor is chain configuration: the side substituents must not hinder regular arrangement of adjacent chains. Large branches make crystallization difficult.

Apart from configuration, the conformational possibilities of a chain are very important for close packing. Close packing is realizable with flexible chains capable of shifting in parts. The introduction into the polymer chain of polar groups gives rise to two opposite effects. On the one hand, intermolecular attraction increases, favouring close packing. On the other hand, the thermo-

dynamic flexibility of the chain decreases. The chain becomes more rigid, making it difficult to move in parts, i.e., making it difficult for a close packing to form. The rate of formation of an equilibrium close packing depends on the magnitude of these two effects. In the case of polar groups (e.g., OH or CN) attraction evidently prevails, and despite considerable chain rigidity such polymers as poly(vinyl alcohol) and polyacrylonitrile form a fairly close packing when cooled. Rigid chains can pack closely only in the extended state, and therefore closely packed polymers with rigid chains are always highly oriented.

However, if the chains are very rigid, close packing may not occur at all. For example, the chains of isotactic polypropylene are very flexible and can form a closely packed crystalline lattice, but rigid cellulose chains cannot form such a lattice under any conditions. As will be shown below, this is a decisive factor in the production of high-strength fibres.

6.4. MECHANISM AND KINETICS OF POLYMER CRYSTALLIZATION

The mechanism of polymer crystallization is the same as that of low-molecular substances; it consists in the formation of crystal nuclei in an amorphous liquid phase and their growth.

It is assumed that when a polymer melt quickly cools to a certain temperature below the melting point, chaotic nucleation occurs, i.e., crystal nuclei originate throughout the entire volume at random places. Nucleation may be homogeneous and heterogeneous.

Homogeneous nucleation consists in the spontaneous aggregation of polymer chains at temperatures lower than the melting point (T_{melt}). Until the critical size of aggregates is attained, this aggregation is reversible, i.e., the aggregates which have been formed are destroyed by thermal motion. When the critical size of aggregates is attained, aggregation becomes irreversible, and the crystal growth begins. Nuclei may appear either instantaneously at the initial moment of crystallization, when a given temperature is attained, or they may originate in the liquid phase during the entire process of crystallization. In the first case, the number of nuclei does not depend on time. In the second case, the following dependence exists:

$$n = Nt \tag{6.2}$$

where n = number of nuclei at an instant t in unit volume
N = nucleation rate.

Heterogeneous nucleation occurs owing to the presence of casual impurities in the liquid phase that are chaotically distributed throughout the volume or are on the surface of a vessel.

The nuclei that have been formed begin to grow. It is taken that the growth of nuclei may be one-dimensional, two-dimensional, and three-dimensional. In this case, rods, discs, and spheres are respectively formed. In the end, the growing elements collide, and the growth stops at the places of their contact: the

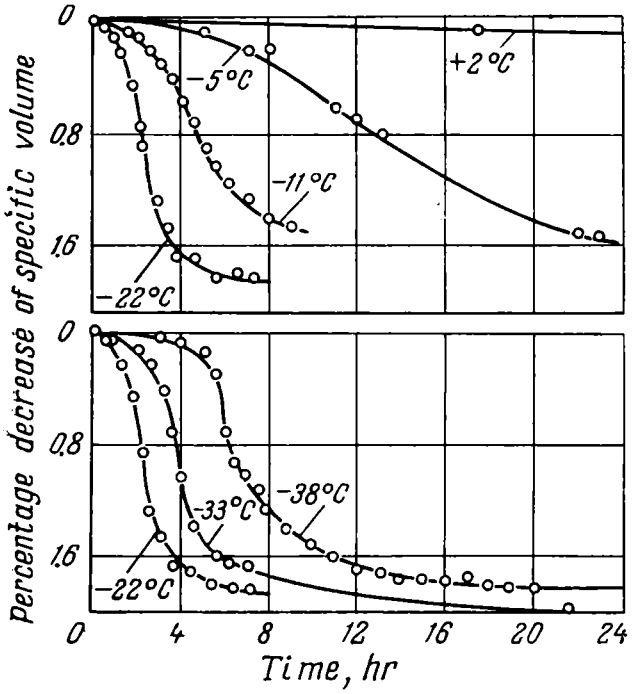


Fig. 6.2. Change in specific volume of rubber with time at fixed temperatures

entire mass transforms into a new phase. The linear dimensions of growing crystal formations increase in time, and it is assumed that

$$r = Gt \tag{6.3}$$

where r = corresponding linear size
G = growth rate.

The overall crystallization rate is determined by the nucleation rate and by the rate of nuclei growth.

The main data on the polymer crystallization rate were obtained by dilatometric measurements, i.e., by measurements of the polymer volume with time at fixed temperatures. Typical graphs of such measurements are given in Fig. 6.2. It follows from the illustration that a change in volume occurs rapidly at a certain temperature range which is characteristic of every polymer, and that the volume of a polymer changes with temperature considerably slower at lower or higher temperatures. These data may

be used to plot a curve of temperature dependence of a polymer crystallization rate. Such a curve for natural rubber is shown in Fig. 6.3. The illustration clearly shows that the crystallization rate versus temperature curve has a maximum, which, for example, for natural rubber corresponds to —25 °C. At this temperature, the entire process of crystallization lasts for five hours. * Such a type of the dependence is determined by two factors which act oppositely: the nucleation and the destruction of nuclei by thermal motion. At sufficiently high temperature, when thermal motion upsets any order, the rate of formation of stable crystal nuclei is naught, and grows with decreasing temperature. However, this growth

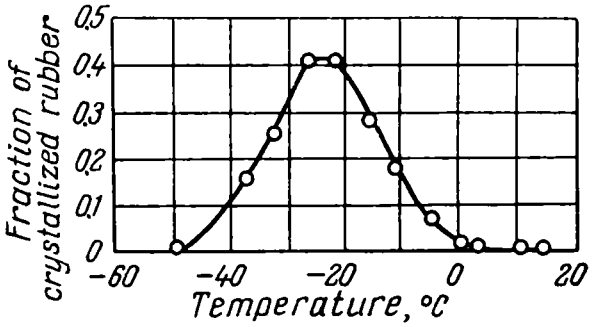


Fig. 6.3. Temperature dependence of crystallization rate of natural rubber

continues to a certain temperature, beginning with which the viscosity of the system sharply increases. This impedes molecule repacking, which is necessary for establishing order. At —50 °C, i.e., at 20 °C higher than the glass-transition temperature of natural rubber, its crystallization rate becomes virtually unnoticeable. This is a characteristic case of supercooling an amorphous substance, since at such a temperature the mobility of the chains and units is too small for crystal formation.

Hence, a glassed polymer cannot crystallize, and the glassy state, being a non-equilibrium state in thermodinamics, may exist infinitely long.

Apart from dilatometry, information on the crystallization and melting of polymers may be quickly obtained by differential thermal analysis (DTA), which consists in the input (or output) of heat to a specimen (or from it) at a given rate, and in the determination of the rate of a process by comparing the temperature of a specimen with that of a standard. When a polymer is melted or crystallized, heat is absorbed or liberated, and these effects are manifested in the form of endothermal and exothermal peaks on a

* This should be borne in mind when storing natural rubber; since crystallized rubber is very difficult to process.

thermogram, whose typical form is given in Fig. 6.4. The curve obtained when heating the specimen testifies to the fact that a polymer melts in the finite range; this will be discussed at greater length on p. 161. The curve for cooling shows that a polymer melt must be considerably supercooled prior to crystallization.

The calorimetric method gives the best information on the heats of melting and crystallization.

The polymer crystallization rate is described well by the Avraami equation proposed by him for low-molecular substances:

$$a = 1 - e^{-K_0 t^n} \qquad (6.4)$$

where a = fraction of a substance which undergoes a phase transition by time t

n = constant which for the given substance characterizes the nucleation type and the growing structure type; it may assume the values of 1, 2, 3, and 4

K_0 = process rate constant.

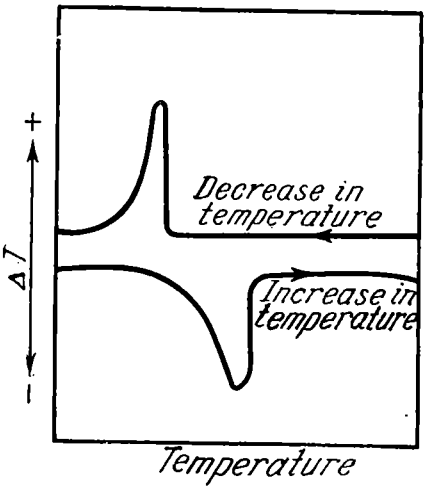


Fig. 6.4. Schematic diagram of DTA curves

The concepts developed by Avraami are applicable to polymers. Although polymers do not undergo a complete phase transformation, Eq. (6.4) describes the kinetics of their isothermal crystallization quite well if a stands for the crystallized part of a polymer.

If the logarithm of Eq. (6.4) is taken twice, we obtain

$$\log[-\ln(1-a)] = \log K_0 + n \log t \qquad (6.5)$$

Hence, a straight line is obtained in the coordinates $\log[-\ln(1-a)]$ vs. $\log t$; the value of n may be determined by its slope, and the value of the constant K_0 may be determined by the segment which it cuts off at the ordinate axis.

The value of $1-a$ represents a fraction of an unconverted liquid polymer, and in the case of dilatometric determination

$$1 - a = \frac{h_t - h_\infty}{h_0 - h_\infty} \qquad (6.6)$$

where h_t = height of the level of liquid at instant t

h_0 and h_∞ = heights of meniscuses that correspond to the beginning and end of a process.

In calorimetric measurements, a stands for the degree of completion of the heat flow, expressing the fraction of a converted substance.

6.5. THERMODYNAMICS OF THE MELTING AND CRYSTALLIZATION OF POLYMERS

Crystallization is a process of transition of a polymer from a disordered state to an ordered one. *Melting* is an opposite process of transition of a polymer from an ordered state to the state of a liquid melt. The melting of polymers is usually regarded as a first-order phase transition. However, owing to the specific structure of polymers, this transition has its own features. For example, low-molecular bodies melt in a narrow temperature range, while polymers melt in a very wide temperature range up to 100 °C.

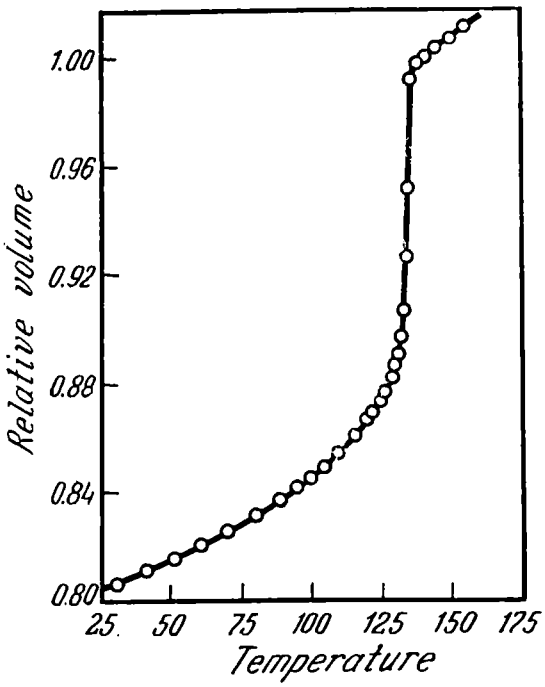


Fig. 6.5. Curve of melting of polyethylene according to the data of the change in volume

The main information on polymer melting and likewise on polymer crystallization was obtained from dilatometric data. Hence, the change in the volume of a crystallized polymer placed in a dilatometer * may be observed when the polymer is slowly heated. A typical dependence of the volume on temperature is given in Fig. 6.5. It is seen from the graph that a change in the polymer volume occurs in a wide temperature range, the degree of polymer crystallinity gradually decreasing.

The process of gradual decrease in the degree of polymer crystallinity is known as *partial melting*, and the temperature at which the traces of crystallinity completely disappear is known as *equilibrium melting temperature* T^0_{melt}.

The temperature range of partial melting depends on the chemical structure of a polymer and on the prehistory of a specimen, and particularly on crystallization conditions, as is illustrated in Fig. 6.6.

If a specimen of natural rubber is crystallized at temperatures ranging from —25 °C to —45 °C, its melting is completed at 0 °C. Specimens which are crystallized at —5 °C melt at temperatures ranging from 0 °C to +16 °C. Specimens which have been in the

* Dilatometer is an instrument for volumetric measurements.

crystallized state for a long time may melt even at higher temperatures, say at 40 °C.

The melting of other crystalline polymers resembles that of natural rubber but at the same time differs from it; for example, the temperature at which polyethylene melts depends to a lesser extent on its crystallization temperature.

There may be several causes of the partial melting of polymers. One of the causes may be the presence of crystals of various size in a polymer. It is known that free surface energy increases

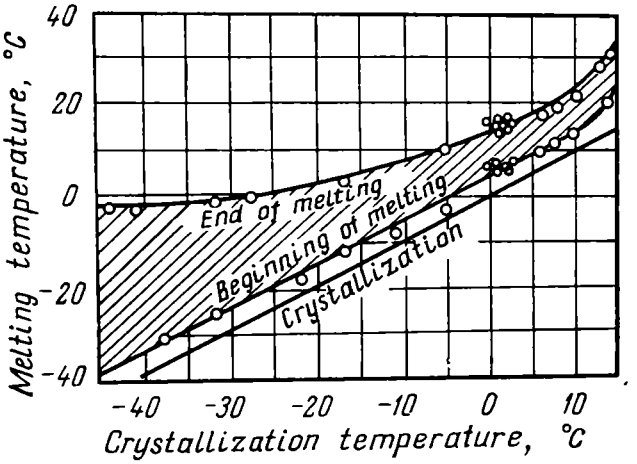


Fig. 6.6. Melting temperature of crystalline rubber as a function of crystallization temperature

when a substance is crushed; this energy is especially great for small crystals. Therefore, they melt at temperatures which are lower than those of larger crystals. However, partial melting is detected also in respect of polymer monocrystals which have a lamellar structure. This melting is the result of both diffusion melting of the faces of lamellar crystallites (or crystalline grains) which are formed by the folds of macromolecules, and the gradual advancement of the melting boundary into a crystallite. The melting temperature of such crystals is connected with the size of a fold l by the relation:

$$T_{\text{melt}} = T^0_{\text{melt}}\left(1 - \frac{2\sigma}{\Delta H_{\text{melt}} l d_{\text{cr}}}\right) \tag{6.7}$$

where σ = specific free energy, or surface tension
ΔH_{melt} = specific heat of melting
d_{cr} = crystal density.

It follows from relation (6.7) that as crystal size increases, T_{melt} grows, and that the greatest melting temperature should be possessed by large crystals. Hence, equilibrium melting temperature may be defined as the temperature of melting of equilibrium

polymer crystals of infinitely large size. It may be determined from the graph of dependence of the experimentally established

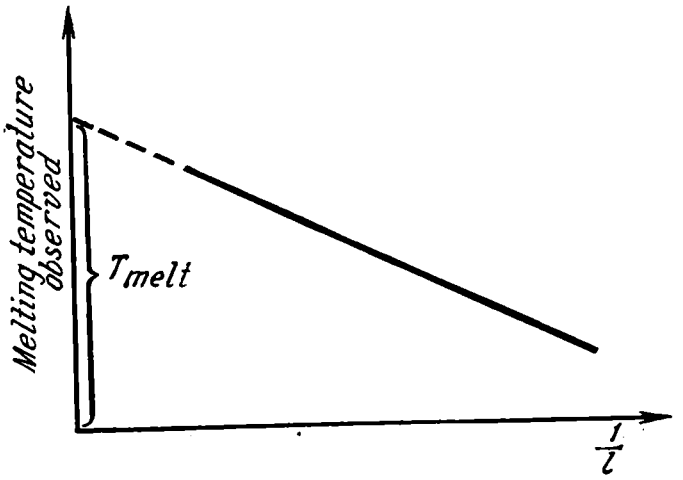


Fig. 6.7. Dependence of the observed melting temperature on the length of a fold of a lamellar crystal

T_{melt} on $\frac{1}{l}$ by extrapolating the straight line to $\frac{1}{l} \to 0$, or $l \to \infty$ (Fig. 6.7).

Another method of determining equilibrium melting point T^0_{melt} consists in representing the graphic dependence of the experimentally determined values of T_{melt} and T_{cr}. This dependence is usually

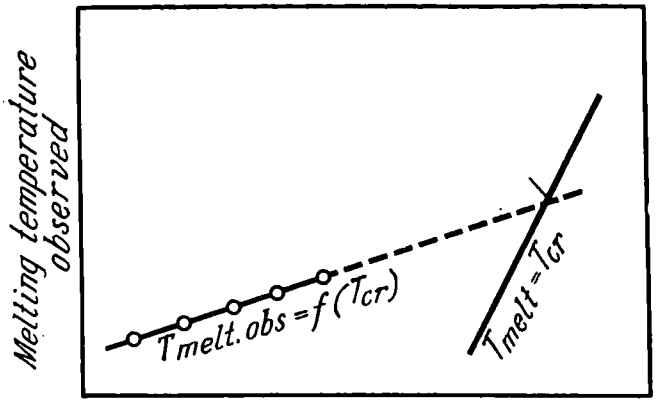


Fig. 6.8. Determining equilibrium melting temperature

rectilinear (Fig. 6.8). The minimum value of melting temperature in every case should be equal to crystallization temperature, since the given specimen cannot melt below its own T_{cr}. The dependence of the minimum melting temperature on crystallization temperature is expressed by straight line. The intersection of these

straight lines gives the value of equilibrium melting temperature. The equilibrium values of T^0_{melt}, being determined by both methods, coincide. Thus, for polyethylene, T^0_{melt} is 145.5 °C.

T^0_{melt} is connected with the enthalpy and entropy of melting by the thermodynamic relation

$$T^0_{melt} = \frac{\Delta H_{melt}}{\Delta S_{melt}} \tag{6.8}$$

The values of these parameters for some polymers are given in Table 6.1, which shows that there is no correlation between the temperature and heat of melting. Hence, polymers may have very high heats of melting and comparatively low melting temperatu-

TABLE 6.1. *Thermodynamic Parameters of Selected Polymers*

Polymer	T_{melt}, °C	ΔH, cal/mole	ΔS, cal/(mole·deg)
Polyethylene	145.5	960	2.07
Polypropylene	176	2 600	5.78
cis-1,4-Polyisoprene (natural rubber)	28	1 050	3.46
trans-1,4-Polyisoprene (gutta-percha)	74	3 040	8.75
Polystyrene	242	2 000	3.88
Poly(decamethylene sebacinate)	80	12 000	34
Poly(decamethylene terephthalate)	138	11 000	27

res. The low values of T_{melt} are usually connected with the high flexibility of chains and the possible formation of a large number of conformations in the molten phase. This leads to high values of the entropy of melting. When the entropy of melting is small, melting temperatures are high.

6.5.1. Melting Temperature of Polymers

The melting temperature of a polymer, like that of a low-molecular substance, depends on the energy of intermolecular interaction (cohesion energy) and on the internal mobility of its molecules, i.e., their ability to undergo conformational changes.

According to present-day ideas a crystal melts when the amplitude of vibration of its atoms or molecules, increasing with rising temperature, reaches a critical value determined by the distance between neighbouring molecules. This occurs at the melting point, and the greater the cohesive energy and the smaller the internal

mobility of its molecules, the higher will this melting point be. The cohesive energies for various groups are given below:

	Cohesive energy, cal/mole		Cohesive energy, cal/mole
$-CH_2-$	680	$-CF_3$	1800
$-CH_3$	1700	$-Cl$	2800
$-C_6H_4-$	3900	—OH (alcohol)	5800
$-C_6H_5$	5400	—COOH	5600
$-CH=CH-$	1700	—CONH—	8500
$-CF_2-$	760	—CONH— (‖ O)	8740

By the order of magnitude they are commensurable with the potential energy barriers (p. 90) determining the internal mobility of the molecules. For this reason the melting point is determined in each concrete case by the ratio of these values. Let us illustrate this by examples:

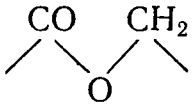
1. Thus, polytetrafluoroethylene has a melting point of 330 °C, and polyethylene, of ca. 135 °C. Low-molecular fluoroparaffins also melt at higher temperatures than the corresponding paraffins. The cohesive energies of the groups $-CH_2-$ and $-CF_2-$ are very close and cannot be the cause of such differences in melting points. At the same time the potential energy barrier for rotation in the CF_3-CF_3 molecule is higher than in CH_3-CH_3 (4350 as compared to 3000 cal/mole). Evidently this difference remains in the polymers.

2. Melting of diene-series polymers also conforms to the regularities observed on melting of their monomeric analogues. For example, the *cis*-isomers of ethylene derivatives are more fusible than the *trans*-isomers. For this reason *trans*-1,4-polyisoprene (gutta-percha) melts at higher temperatures than the *cis*-1,4-isomer (natural rubber). The melting point of *cis*-1,4-polybutadiene is 1 °C, whereas that of *trans*-1,4-polybutadiene is 148 °C. Apparently the lower melting points are due to greater polymer chain flexibility.

3. The effect of internal mobility of molecules on the melting point T_{melt} of a substance can be illustrated on low-molecular polyphenylenes. Thus, despite the possibility of torsional vibrations of individual rings about the C—C bond, the number of conformations in the *p*-polyphenylene molecule is not large, and its chain is comparatively rigid. If the rings are connected in the *meta*-position, the number of conformations the chain can acquire increases. This accounts for that T_{melt} of *p*-pentaphenylene (395 °C) is much higher than that of *m*-pentaphenylene (112 °C).

4. Strong effect of chain flexibility on melting point is observed in polyethers. Substitution of oxygen or sulphur for a $-CH_2-$

group in the polymer chain lowers the melting point despite an increase in cohesive energy. This applies both to monomers and polymers. All polyethers have lower T_{melt} than polymethylene, due to the insignificant potential energy barrier for rotation about the direction of C—O—C and C—S—C bonds and the resulting increase in chain flexibility of polyethers. With a high sulphur content the cohesive energy becomes dominant, and T_{melt} rises.

5. Aliphatic polyesters also melt at lower temperatures than polymethylene in spite of the presence in them of the polar groups —C(=O)—O—, capable of forming intermolecular hydrogen bonds. Note that low-molecular esters such as dibutyl adipate and butyl valerate also have lower melting points than the corresponding hydrocarbons. At the same time monomeric ketons melt at slightly higher temperatures. All these facts are evidence that the low melting points of polyesters are due to the presence of flexible C—O—C bonds in their chains. If for some reason rotation about the direction of the C—O—C bond is hindered, the melting point rises. Let us compare the behaviour of poly(ethylene adipate) with that of poly(ethylene terephthalate). In the latter's crystal the ester group  is in a plane, whereas in the poly(ethylene adipate) molecule the CH_2 group is turned by 80° about the C—O—C bond, i.e., the arrangement differs considerably from planar one. This facilitates rotation about the direction of this bond. Rotation in the poly(ethylene terephthalate) molecule is very difficult. For this reason its melting point is 100 °C, which is higher than that of poly(ethylene adipate) (50 °C).

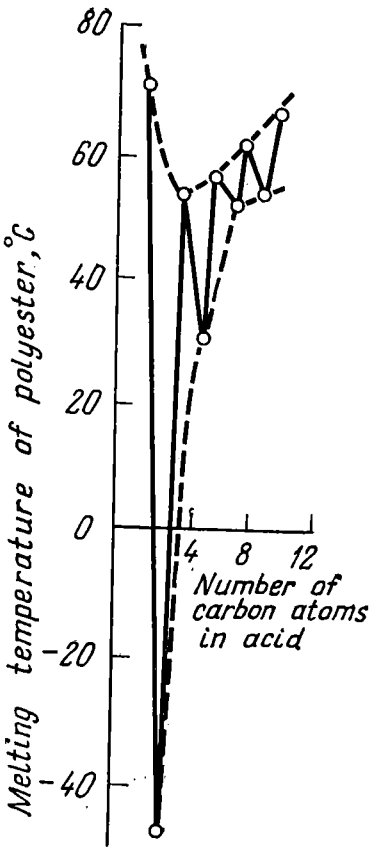


Fig. 6.9. Dependence of the melting point of polyesters on the number of carbon atoms in the acid

6. If the ester groupings in the macromolecular skeleton are replaced by amide groups, chain flexibility decreases and cohesive energy sharply increases, resulting in a major rise of T_{melt} of polyamides compared to the melting points of polyesters. The melting points of polyurethanes, which contain both amide and ester

groups in their chains, are intermediate between those of polyesters and polyamides.

The series polyesters, polyamides, and polyurethanes display a regularity well known in organic chemistry, namely, a difference in melting points of compounds with even and odd numbers of carbon atoms. This regularity is manifested even in the normal paraffin series. With increasing molecular mass the melting points of paraffin hydrocarbons rise, asymptotically approaching a certain limiting value. The curve for hydrocarbons with an even number of carbon atoms runs higher in this case than for hydrocarbons with an odd number of carbon atoms. The temperature difference between the curves is only a few degrees, but increases sharply for molecules having on both ends bulky groups capable of forming strong intermolecular bonds, e.g., COOH groups. Thus, in the lower dicarboxylic acids series melting point decreases with increasing molecular mass, and the larger the number of CH_2 groups, the smaller will be the difference in melting points between adjacent members of the homologous series. Compounds with even numbers of carbon atoms melt at higher temperatures than those with odd numbers of them. For example, oxalic acid melts at 189.5°, malonic at 133°, succinic at 153°, glutaric at 97.5°, pimelic at 105 °C, etc.

The same regularity is observed in polymer series (Fig. 6.9). Polyethers, polyesters, and polyamides with even numbers of carbon atoms in their dicarboxylic acid, dihydric alcohol, or diamine residues have higher melting points than compounds with odd numbers of carbon atoms. Bunn relates this phenomenon to the fact that the thermal vibrations of molecules in crystals evidently differ depending on the evenness or oddness of the number of carbon atoms in the chain.

6.6. FREE VOLUME AND PACKING DENSITY OF POLYMERS

The properties of polymers, like all low-molecular substances, are determined not only by the nature of atoms composing a molecule and by the mutual arrangement of the latter in space, but also by the distance between them; the energy of intermolecular interaction and the mobility of the elements of a structure are dependent on this distance. The presence of certain intermolecular distances leads to the fact that some space or volume of a body remains unoccupied by its mass. This part of the volume has become known as the *free volume* of a substance in contrast with the *occupied volume*, or *proper volume* of the molecules themselves.

It will be seen further that many theories are based on the concept of free volume; however, different authors understand it differently. Hence, the distinction is made between:

1. *Free volume*, which is equal to the difference between the molar volume of a body at a given temperature V_T and the volume of one mole of it at absolute zero V_0, presupposing a crystalline packing:

$$V_f = V_T - V_0 \tag{6.9}$$

This concept was introduced by Frenkel who wrote about "excess volume of a body in comparison with that at absolute zero".

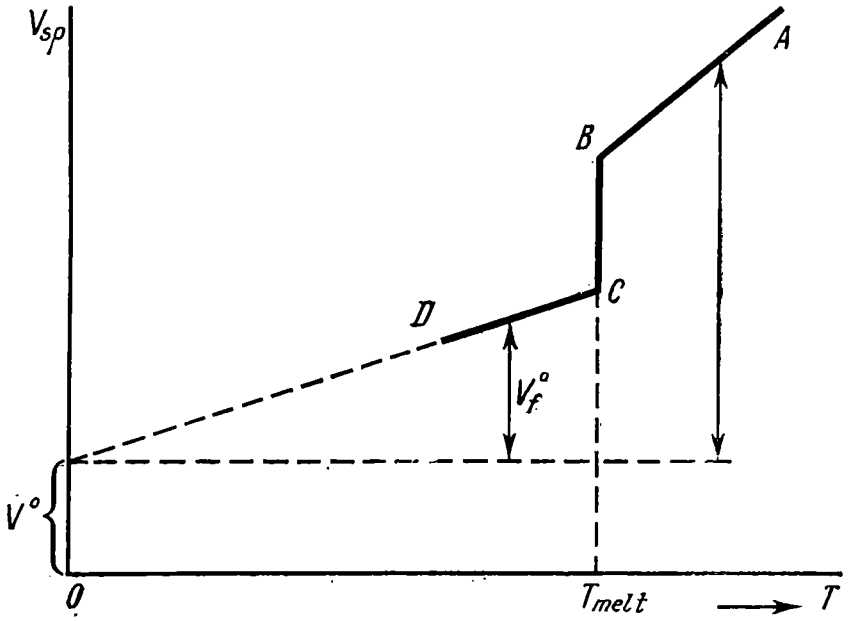


Fig. 6.10. Change in the specific volume with temperature

2. *Empty volume* V_E, which is equal to the difference between the volume of one mole of a body at a given temperature and the proper volume of its molecules V_w:

$$V_E = V_T - V_w \tag{6.10}$$

3. *Fluctuation volume*, which is the product of the volume formed as a result of deviations of molecules from its centre of gravity ΔV_a upon thermal motion by the number of molecules in one mole (N_A):

$$V_{fl} = N_A \Delta V_a \tag{6.11}$$

The value of V_{fl} is very small in comparison with V_E and V_f.

The free volume, or the "excess volume of a body over its volume at absolute zero", may be estimated by determining the temperature dependence of the specific volume of a body. This dependence is illustrated in Fig. 6.10.

Straight line AB corresponds to a change in the specific volume of a liquid with temperature. At point B, phase transition occurs, i.e., a crystalline phase is formed, and the volume changes jumpwise to point C (crystal volume). On further cooling, the volume changes along the straight line CD, which slopes less than the straight line AB, i.e., the crystal volume changes with temperature slower than the liquid volume since, when a crystalline body is heated, only the amplitude of oscillations of atoms changes relative to their equilibrium positions, and when a liquid is heated,

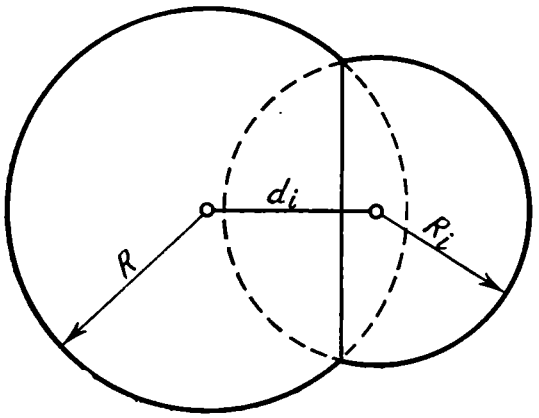


Fig. 6.11. Scheme of the formation of chemical bond between two atoms

the equilibrium positions themselves also change, leading to more noticeable changes in the volume. It may be assumed that the temperature coefficient of expansion will remain the same up to absolute zero, and the straight line CD may be extrapolated up to $T = 0$. The difference between the volume of a body at a given temperature and the volume at absolute zero V_0 is the free volume V_f.

There are also other methods of estimating the value V_0. The values of V_0 for low-molecular liquids obtained by them differ by 2-3 per cent. Therefore, it may be considered that for liquids, the values of V_0 are established, and consequently V_f may be calculated. For polymers, it is considerably more difficult to determine V_0, since many methods cannot be used. When an attempt is made to extrapolate the values of volumes or densities of a polymer, difficulties arise in connection with the glass transition of a polymer (p. 149). Haward believes that the most accurate data may be obtained by calculating the internal pressures of a polymer; this requires measurements at high pressures at temperatures higher than T_g of a polymer. Such measurements were undertaken by Rehage and Breuer. For polystyrene, they obtained the value $V_0 = 0.82\text{-}0.85$ cm^3/g or 85-88 cm^3 per basic mole.

To determine the empty volume V_E, it is necessary to know the proper volume of molecules, which may be estimated on the basis of both the volumes of atoms and atomic groupings composing a given molecule and their number. These increments, or constituent volumes, are calculated in the following way.

According to the concepts of crystal chemistry, the volume of an atom is described by a sphere with the intermolecular (van der Waals) radius R. If a given atom is chemically bound with other atoms, both atoms cut off parts of spheres from one another (Fig. 6.11). The interatomic distance is equal to the length of a chemical bond d_i, which is always smaller than the length of an intermolecular bond. The volume, or "increment of volume", of an atom ΔV_i is calculated as the difference between the volumes of the sphere of this atom and the volumes of spherical segments, which are cut off from the given sphere by adjacent atoms that are bound with it by valence:

$$\Delta V_i = \frac{4}{3}\pi R^3 - \sum_i \frac{1}{3}\pi h_i^2 (3R - h_i) \qquad (6.12)$$

here h_i is height of a segment, which is calculated by the formula

$$h_i = R - \frac{R^2 + d_i^2 - R_i^2}{2d_i} \qquad (6.13)$$

where R = intermolecular radius of an atom
d_i = length of a bond between two atoms
R_i = intermolecular radii of adjacent atoms which are bound by valence.

All these values have been determined by X-raying of crystals.

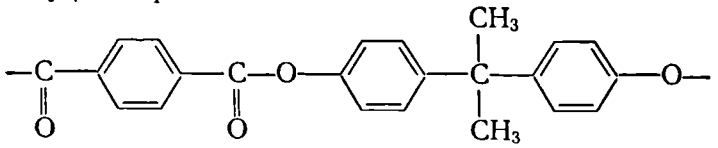
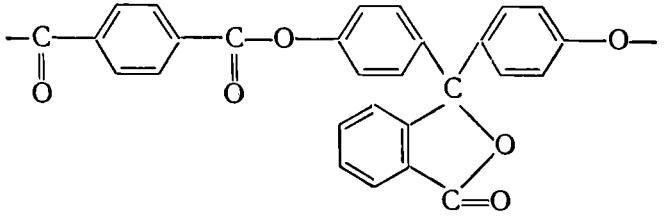
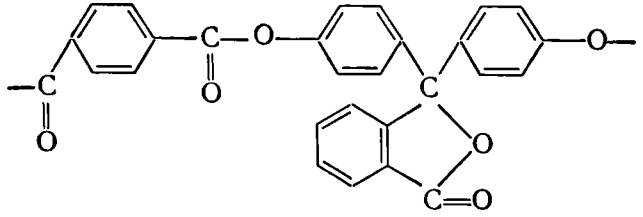
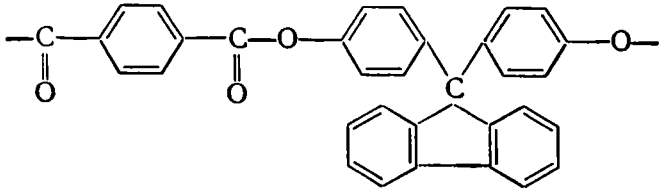
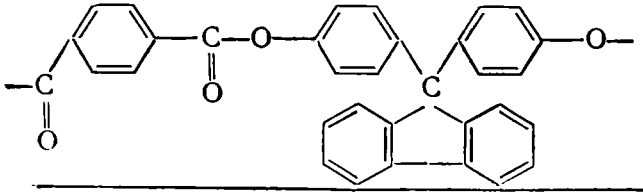
Equations (6.12) and (6.13) were used to calculate the values ΔV_i for many atoms and atomic groupings.

The proper volume of a unit of a macromolecule is calculated as the sum of the increments of the volumes of groupings which are included in it. For example, the proper volume of a unit of a polystyrene chain is the sum of the increments of the volumes of one group of CH_2, five aromatic groups of CH, one aromatic atom of carbon, and one aliphatic group of CH, which is connected to the aromatic nucleus.

The calculated values of V_f and V_E for the same polymer naturally do not coincide; however, every interpretation of free volume is based on the concept of "space", which is given to molecules or atoms for their motion. On melting, this space usually increases by 10 per cent, this increase in free volume being enough to create space that is required for flow. In addition, the free volume of a liquid and that of crystals differ by their nature. The free volume or empty volume of a crystal is due to the existing looseness in molecule packing, constituting 20-30 per cent of even

TABLE 6.2. *Characteristic of Packing Density of Polymers*

Polymer	Phase state	Density d, g/cm³	V_T cm³/mol	V_W cm³/mol	V_E cm³/mol	K
Polyethylene	cryst.	1.000	28.0	20.6	7.4	0.735
Polyethylene	amorph.	0.92 (19)	30.4	20.6	9.8	0.676
		0.855 (20)	32.7	20.5	12.2	0.625
Polypropylene	cryst.	0.95 (20)	44.2	30.6	13.5	0.694
Polypropylene	cryst.	0.936 (19)	44.8	31.1	13.7	0.693
Polyisobutylene	cryst.	0.937 (19)	39.7	41.6	18.1	0.696
Polyisobutylene	amorph.	0.86 (20)	65.1	40.9	24.2	0.628
Polyisoprene	cryst.	1.000 (19)	68.0	49.3	18.7	0.725
Polyisoprene	amorph.	0.92 (19)	73.4	49.3	24.1	0.667
Polystyrene	cryst.	1.12 (19)	92.8	66.0	26.8	0.710
Polystyrene	amorph.	1.05 (19)	99.0	62.8	33.2	0.634
Polyvinyl alcohol	cryst.	1.26 (20)	34.2	25.0	9.8	0.717
Polymethyl methacrylate	amorph.	1.169 (19)	85.5	58.5	27.0	0.684
Polyethyl methacrylate	amorph.	1.124 (19)	101.4	69.1	32.3	0.680
Polypropyl methacrylate	amorph.	1.078 (19)	118.7	76.6	41.9	0.646
Polybutyl methacrylate	amorph.	1.055 (19)	134.6	89.6	45.0	0.665

Poly-*p*-benzamide	cryst.	1.488 (22)	79.9	63.6	16.3	0.796
Poly-*p*-terephthalamide	cryst.	1.503 (22)	158.3	126.1	32.2	0.796
	amorph.	1.195 (19)	210.8	144.3	66.5	0.679
	amorph.	1.307 (19)	342.7	234.7	108.0	0.685
	amorph.	1.296 (19)	348.1	234.7	113.4	0.679
	amorph.	1.244 (19)	385.4	263.4	122.0	0.683
	amorph.	1.239 (19)	387.4	263.4	124.0	0.680

ideal crystalline bodies, and also to the anharmonicity of oscillations of atoms relative to equilibrium positions, i.e., the fluctuation volume. In liquids, the equilibrium positions themselves are displaced, leading to the formation of microcavities, or "holes", which are distributed nonuniformly throughout the volume. These "holes" have a fluctuation nature, i.e., they continuously originate and disappear under the action of thermal motion. They are very small, but their volume grows as the temperature rises and approaches the boiling point.

Packing coefficient. The empty volume calculated by Eq. (6.10) is directly connected with the packing coefficient K, which is the ratio of the proper volume of molecules to the volume of one mole of a body at a given temperature:

$$K = \frac{V_w}{V_T} = \frac{N_A \sum \Delta V_i}{V_T} = \frac{N_A \sum \Delta V_i}{M/d}; \quad 1 - K = \frac{V_E}{V_T} \qquad (6.14)$$

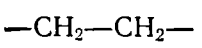
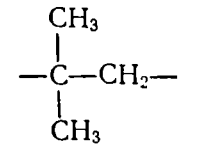
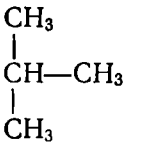
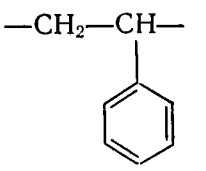
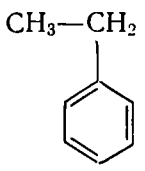
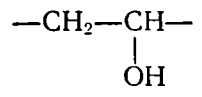
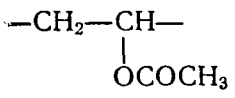
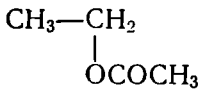
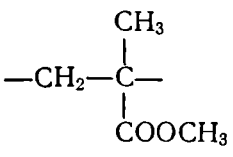
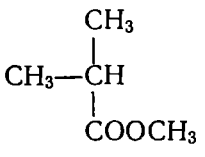
where d = density of a body
M = molecular mass.

Polymer packing coefficients had been calculated for the first time by Kitaigorodsky and recently more accurate calculations were made by Slonimsky and Askadsky. The values of V_E and K for some polymers are given in Table 6.2. It is evident that the packing coefficients of crystalline polymers are within the same limits as K of ordinary crystalline bodies (0.68-0.80) and depend on the chemical nature of a polymer. The empty volume in polymer crystals is approximately 0.20-0.35 cm^3/g. The packing coefficients of monolithic amorphous polymers are, by their value, close to the lower boundary of K of crystalline bodies, and are virtually independent of the chemical nature of a polymer. However, K of real amorphous polymers may be considerably lower and depend on their chemical nature (Table 6.2).

A more sensitive characteristic of polymer packing density is the value of compression or contraction, which is always observed in polymerization or polycondensation. In these processes, monomer molecules, which have been at distances characteristic of intermolecular bonds (3-4 Å), begin to acquire the distances of chemical bonds ($\sim$1.54 Å). It follows that the processes of polymerization and polycondensation are always accompanied with an increase in density or a decrease in free volume. Therefore, the *free volume of a polymer is always smaller than the free volume of a monomer.*

However, it is not quite correct to compare the densities of polymer and monomer, because the monomer contains double bonds, which are absent in the polymer chain, and the distances between C=C and C—C carbon atoms are different. Hence, it is more

TABLE 6.3. *Polymers and Their Corresponding Hydrogenated Monomers*

Polymer		V_{pol}	Hydrogenated monomer		$V_{h.\ mon.}$
name	repeating unit		name	formula	
Polyethylene		30.6	Ethane	$CH_3—CH_3$	89.6
Polyisobutylene		61.6	Isobutane		105
Polystyrene		98	Ethylbenzene		122.6
Poly(vinyl alcohol)		34.3	Ethyl alcohol	$CH_3—CH_2OH$	55.8
Poly(vinyl acetate)		72.2	Ethyl acetate		98.5
Poly(methyl methacrylate)		82.4	Methyl isobutyrate		1148

correct to compare the densities and volumes of the polymer with those of its hydrogenated monomer (hydrogenated polymer unit), which is the low-molecular analogue of the polymer in question.

Table 6.3 gives the chemical formulas for the repeating units of some polymers and of their corresponding hydrogenated monomers, and Table 6.4 lists the ΔV values and the packing factors of some selected polymers, recalculated for the hydrogenated monomer.

TABLE 6.4. *Change in Density and Volume Upon Polymerization*

Polymer	Density, g/cm³		Molar volume		$\Delta V = V_{pol} - V_{h.mon}$
	hydrogenated monomer	polymer	$V_{h.mon}$	V_{pol}	
Polyethylene (amorphous)	0.335	0.92	89.6	30.6	—59
Polyisobutylene	0.553	0.91	105	61.6	—43.4
Polyisoprene (amorphous)	0.6627	0.91	106	75	—31
Poly(vinyl alcohol)	0.7892	1.3	55.8	34.3	—21.5
Poly(vinyl acetate)	0.8945	1.191	98.5	72.2	—26.3
Poly(methyl methacrylate)	0.8906	1.19	114.8	84.2	—30.6
Polystyrene	0.8669	1.057	122.6	98	—24.6
Polydihydronaphthalene	0.9732	1.14	136	114.3	—21

The value of compression is calculated as follows:

$$\Delta V = V_{pol} - V_{h.\,mon} \qquad (6.15)$$

where V_{pol} = molar volume of a polymer

$V_{h.\,mon}$ = molar volume of a hydrogenated monomer.

However, as it follows from Table 6.4, the values of ΔV greatly vary for different polymers. This is because the contraction or compression which occurs in the polymerization process is due to two causes, one of which has been discussed: it is the replacement of intermolecular distances with the distances of the chemical bond. However, there is another cause of contraction: the denser packing of polymer chains in comparison with the packing of small molecules. This is evident from the fact that the packing coefficients of polymers are always greater than those of monomers ($K_{pol} > K_{mon}$).

Let us represent a general contraction ΔV_{gen} in the form of a sum of two quantities: $\Delta V'$—contraction due to the replacement

of intermolecular bonds with chemical bonds, and $\Delta V''$—contraction due to denser chain packing:

$$\Delta V_{gen} = \Delta V' + \Delta V'' \tag{6.16}$$

The relative fraction of each type of contraction is determined by the relations

$$\alpha' = \frac{\Delta V'}{\Delta V_{gen}}; \qquad \alpha'' = \frac{\Delta V''}{\Delta V_{gen}} \tag{6.17}$$

The quantities α' and α'' have been calculated recently, and it has been ascertained that in all cases the smaller fraction of contraction is due to the opening of double bonds, and the larger one, to the dense packing of polymer chains. The chemical structure of a polymer considerably affects the quantities α' and α''. The least dense packing of chains (the smallest fraction of α'') is observed in polystyrene; it follows that this polymer is packed the least densely. The quantities α' and α'' of polyvinyl acetate and polymethyl methacrylate, which is isomeric to it, are approximately the same. In the polymethacrylate series, the relative fraction of contraction of α'' is always larger than in the polyacrylate series, indicating a denser packing of the first-series chains. In both polymer series, as the volume of the side substituent grows, α'' increases and then decreases. A decrease in the effect of the dense packing of chains is in all probability due to steric hindrances.

The data of Table 6.3 show that polymers have different packing density, which depends on the structure of their chains, particularly on the dimensions of the substituents. When the structure of macromolecules is the same, the packing density of a crystalline polymer is greater than that of an amorphous one. In this case, a comparison may be made of the values of their densities given in Table 6.4.

6.7. AMORPHOUS POLYMERS

Hence, many polymers incapable of crystallization are in an amorphous state, i.e., in a state which does not possess a crystalline lattice. Owing to the slow kinetics of the crystallization process, crystallizable polymers may supercool and likewise pass over to an amorphous state, which is consequently a very common state for polymers.

Depending on temperature, amorphous low-molecular substances may be in two states of aggregation: *glassy* and *liquid*. Depending on temperature, amorphous linear polymers may be in three physical states: glassy, rubber-like, and viscofluid.

The *glassy state* is characterized by vibrational motion of the atoms constituting the chain about an equilibrium position. There is practically no vibrational motion of units, or movement of the chain as an integral whole. The *rubber-like state* is characterized by vibrational motion of units (torsional vibrations), as a result of which the polymer chain becomes flexible (see Chap. 4). The *viscofluid state* is characterized by mobility of the entire macromolecule as a whole.

When a polymer is heated, its units acquire vibratory motion first, the chains beginning to move only at a higher temperature. Hence, with rising temperature an amorphous linear polymer passes from the glassy to the rubber-like, and then to the viscofluid state. On lowering of the temperature the polymer passes through all three states in the reverse order.

Transition of a polymer from one state of aggregation to another does not occur at any definite temperature, but within a certain temperature range; this is accompanied by a gradual change in its thermodynamic properties. The average temperatures of transition regions are called *transition temperatures.* The temperature of transition from the glassy to the rubber-like state (and vice versa) is the *glass* or *glass-transition temperature* T_g; the temperature of transition from the rubber-like to the viscofluid state (and vice versa) is the *flow temperature* T_f.

These three aggregation states are possible both in crystallizing and in *noncrystallizing* polymers.

Below and above the glass-transition temperature a polymer is in the same phase state, namely, *the amorphous.*

Polymers are characterized by a rubber-like state, which will be dealt with in Chap. 7. In Chapter 8, the regularities of the transitions of polymers from a rubber-like state to glassy and viscofluid states are examined in detail.

6.8. PRACTICAL IMPORTANCE OF THE THEORY OF PHASE AND AGGREGATION STATES OF POLYMERS

The theory of phase and aggregation states of polymers is of great practical importance in processing and in the use of polymeric materials. The mutual arrangement of chains determines all the mechanical characteristics of fibres, films, rubbers, and plastics, and the task of producing polymeric materials with tailor-made properties depends to a very great extent on the structure imparted to the material during processing.

Plastics and fibres are employed in the solid state — crystalline or glassy (amorphous). Above the melting point or glass temperature they become soft. For this reason their melting or glass

temperatures mark the upper temperature limit of their service properties, or their *heat resistance.*

In the case of plastics and fibres the glass or melting temperatures should be much higher than the temperature at which they are used. For instance, the glass temperature of a plastic should be 60-80 °C higher than the temperature at which it is employed.

Various goods made of rubber are used in the rubber-like state. For these polymers the glass or crystallization temperature is in a number of cases the lower temperature limit of their serviceability and determines the *frost resistance* of such materials. Below this temperature the polymer is in the solid state and is unsuitable for use. Hence, the glass transition or crystallization temperature of rubbers must be as low as possible. The glass temperature of modern high-quality, so-called frost-resistant rubbers is between —70 and —90 °C. Rubbers with glass temperatures of —20 to —40 °C are considered nonfrost-resistant. If glassy or crystalline plastics are heated above the glass or melting temperature, they acquire rubber-like properties, and rubbers harden when cooled.

The ability of polymers to pass into the viscofluid state is of great importance for their processing. In most cases polymers are fabricated (moulded) into articles while in the viscofluid state.

Thus, to select the proper conditions of processing and usage of polymeric materials it is necessary to know the specific behaviour of polymers in the crystalline, glassy, and rubber-like states and the regularities governing their transition from one state of aggregation into another.

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CHAPTER 7

Rubber-Like State of Polymers

A rubber-like state is a state in which a polymer is capable of undergoing very great recoverable deformations that occur under the influence of very small loads. This phenomenon has become known as rubber-like elasticity, since it appears in natural rubber.

Great recoverable deformations are known as *rubber-like* deformations, and the bodies which are capable of undergoing such deformations are rubber-like materials, rubbers, elastomers and elastics. Thus, rubber may recoverably straighten by 700 per cent, i.e., by eight times its original length. This is 1000 times greater than the elastic deformability of ordinary solids. To elongate a 1 mm steel wire by 1 per cent, a 160 kgf load is needed, and to elongate a rubber thread of the same diameter, a load of 0,001 kgf is enough. It follows that rubber considerably differs from ordinary solids. According to some indices, it is close to liquids (Table 7.1). However, rubber differs from liquids by other properties. Therefore, the rubber-like state of polymers should be regarded as a particular state of matter that is inherent only in polymers under certain conditions.

To get an insight into the physical essentials of rubber-like state let us consider some well-known types of deformation.

TABLE 7.1 *Volume Expansion Coefficients and Compressibility*

Substance	Volume expansion coefficient	Compressibility, $cm^2/dyne$
Gases	4×10^{-3}	10^{-6}
n-Hexane	11×10^{-4}	16×10^{-11}
Rubber	6.6×10^{-4}	5.1×10^{-11}
Solid (iron)	3×10^{-5}	7×10^{-13}

7.1. ELASTIC DEFORMATION

The ability of bodies to recover their initial shape after removal of the external forces deforming them is called *elasticity.* If the body recovers its shape completely, it is called *elastic.*

The basic law of deformation of an ideally elastic body is Hooke's law, according to which the strain of a body per unit length is directly proportional to the applied stress.

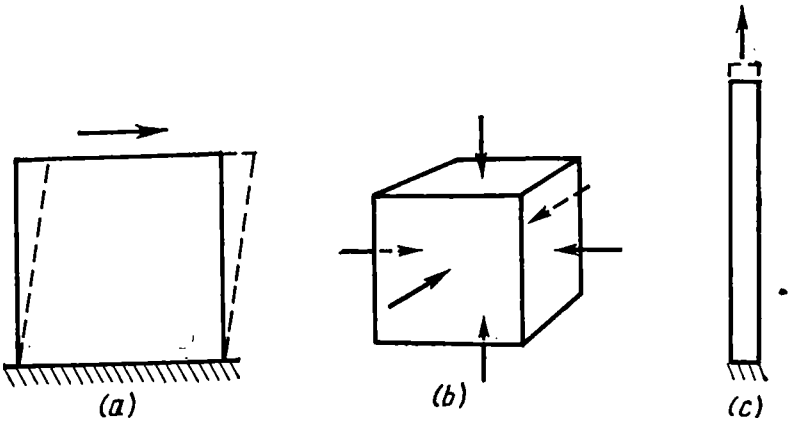

Fig. 7.1. Schematic representation of deformations:
a—simple shear; *b*—uniform compression; *c*—simple extension

Two kinds of stress are distinguished: normal σ_n and shear (tangential) σ_{sh}. The former arises during extension and compression, and the latter, during shear. We shall now discuss this in greater detail.

The simplest kinds of strain are simple shear and bulk or uniform compression (or extension).

Simple shear is illustrated by Fig. 7.1*a*. If a rectangular block is deformed by a shear stress σ_{sh}, only the shape of the specimen will change, but not its volume. The shear strain depends on the tangent of the angle γ formed by the upper plane shifting with respect to the lower, or on the angle itself, if it is small. The shear or rigidity modulus

$$G_{sh} = \frac{\sigma_{sh}}{\gamma}. \tag{7.1}$$

Bulk Compression. If each face of a cube is subjected to a normal force (Fig. 7.1*b*), the compressive stress will be the pressure P. This will cause a change in volume of the specimen, but not in its shape. The volume strain is the decrease in volume per unit volume $-\Delta V/V$. The modulus of uniform compression or bulk modulus

$$K = -\frac{P}{\Delta V/V} \tag{7.2}$$

All the other kinds of strain are more complex since both shape and volume of the body change. Thus, *simple extension* of a rod of cross-sectional area A (Fig. 7.1*c*) by a normal force applied to its ends involves both longitudinal strain ε_{long} and lateral compression ε_{lat} * of the sample. The modulus of elasticity, or Young's modulus, equals

$$E = \frac{\sigma_u}{\varepsilon_{long}} \tag{7.3}$$

The absolute value of the ratio of the lateral strain to the longitudinal strain is called Poisson's ratio:

$$\mu = \left| \frac{\varepsilon_{lat}}{\varepsilon_{long}} \right| \tag{7.4}$$

Poisson's ratio is a dimensionless quantity serving as a measure of the lateral compression accompanying longitudinal extension. The modulus of elasticity is related to the shear modulus by the expression:

$$1 + \mu = \frac{E}{2G_{sh}} \tag{7.5}$$

For bodies with $\mu = 0.5$

$$E = 3G_{sh} \tag{7.6}$$

If Eqs. (7.1) and (7.3) are satisfied, the dependence σ vs. ε is represented graphically over the entire range of stresses and strains by a straight line passing through the coordinate origin. In this case the values of G_{sh} and E are constant and fully characterize the properties of the material.

The reciprocal of the modulus of elasticity is called *compliance*. In simple shear the compliance $I = 1/G_{sh}$; in bulk compression the volume compliance $B = 1/K$. In simple extension the compliance $D = 1/E$.

Bodies possessing elastic properties fall into two groups. Bodies of the first group strongly resist changes in shape and deform recoverably to an insignificant extent. They may be either amorphous or crystalline in structure. The second group includes bodies which change their shape readily and are capable of recover-

* $\varepsilon_{ext} = \frac{l - l_0}{l_0} = \frac{\Delta l}{l_0}$, where l_0 = initial length of specimen, l = length of deformed specimen. The quantity $\varepsilon_{comp} = \frac{h - h_0}{h_0} = \frac{\Delta h}{h_0}$, where h_0 = initial height of specimen; h = height of specimen under load.

able deformations of several hundred per cent. Examples are gases and rubbers.

Atoms, molecules, or ions are always spaced in the crystalline lattice at distances whereat attraction forces are balanced by repulsive forces. The application of external forces will disturb this equilibrium. If the external forces tend to draw the atoms or ions apart, forces of attraction arise between them, counteracting the external forces. If the external forces tend to bring them closer together, repulsive forces arise. Hence, the external deforming forces do work in overcoming the internal forces of interaction, i.e., the elasticity of a crystal is *energetic by its nature.*

Since the interaction energy in crystals is very high, crystalline bodies offer great resistance to changes in shape. Even if very large stresses are applied, they deform very little, i.e., possess a small elastic strain.

Owing to the low mobility and close packing of the atoms and molecules of glassy low-molecular bodies, the energy of interaction between their atoms and molecules is very high, and therefore the elastic strain of such bodies is also very small.

Not only solids possess elastic properties. If a gas is compressed in a closed vessel, its pressure increases, i.e., the gas offers resistance to the external forces compressing it. Hence, a gas is an elastic body possessing volume elasticity. The elasticity of a gas is due to the thermal motion of its molecules, i.e., is of a *kinetic nature.*

The physical sense of the elasticity modulus of a gas can be demonstrated in the following way. An ideal gas contained in a cylinder at temperature T and pressure p occupies the volume $V = Sl$ (where S is the cross-sectional area of the cylinder and l its height). Since the gas is ideal ($pV = RT$), the change in its volume and pressure upon isothermal compression (shift of the piston over a distance dl) is described by the equation

$$p\,dV + V\,dp = 0 \tag{7.7}$$

Hence,

$$dp = -p\frac{dV}{V} = -p\frac{S\,dl}{Sl} = -p\frac{dl}{l}$$

or

$$dp = -pz \tag{7.8}$$

where $z = \frac{dl}{l}$.

Equation (7.8) essentially corresponds to Hooke's law, the pressure increment dp playing the part of the counteracting force, and the initial pressure of the gas p, that of the elasticity modulus.

The moduli of elasticity for some materials are given below (kgf/mm^2):

Steel	20 000-22 000
Platinum	16 000-17 500
Copper	10 400
Zinc	8000-13 000
Quartz	8000-10 000
Polymers (in the rubber-like state)	0.02
Gas	0.01

The modulus of elasticity depends on the nature of the elastic forces. Bodies with energetic elasticity (metals, minerals) possess large elasticity moduli. Gases have very low elasticity moduli owing to the kinetic nature of their elasticity.

The different nature of elastic forces affects the temperature dependence of the modulus and the heat effect of deformation.

Raising the temperature of a crystal increases the distances between its ions or atoms due to an increase in intensity of vibration about their equilibrium positions, and thus weakens the forces of interaction between them. Hence, a smaller stress is needed to cause the same strain at elevated temperature. This means that the modulus of elasticity of a crystal decreases with rising temperature.

In gases, raising the temperature increases the intensity of thermal motion of its molecules and increases its pressure. Hence, the elasticity modulus of a gas increases with rising temperature.

Deformation of crystalline bodies always involves a drop in temperature; after the straining forces are removed and the body has recovered its initial shape its temperature rises again. Deformation (compression) of a gas involves heating; after the external forces are removed the gas expands and cools.

7.2. IRRECOVERABLE FLOW DEFORMATION

Besides recoverable (elastic) deformation there is also irrecoverable flow deformation.

Flow is irrecoverable displacement of the molecules of a substance relative to one another under the action of an external stress; during flow internal friction arises in the substance, counteracting displacement of the molecules. Flow is observed in gases, liquids, and crystalline bodies, but the nature of the internal friction forces differs in the different phases and physical states of matter.

In the gaseous state, owing to large intermolecular distances the interaction forces between the molecules have little effect on their mobility. The molecules are mainly in a state of free transla-

tional rectilinear motion and change their velocities and directions only when they collide. Collisions between molecules involve an exchange of momentum between layers moving at different velocities which is the cause of internal friction. Hence, internal friction in gases is due to the thermal motion of their molecules; in other words, it is *kinetic by its nature.* Raising the temperature increases the number of collisions between molecules and thus increases internal friction.

In crystals, translational motion of atoms and molecules is difficult. Flow can occur by displacement of planes of the crystalline lattice relative to one another, this involves overcoming the interaction forces between the planes, which hinder flow. Hence, the internal friction of crystalline bodies is *energetic by its nature.*

The mobility of molecules in the liquid state is approximately the same as in gases, but owing to much closer packing the molecules interact with one another, and to move them the forces of intermolecular interaction have to be overcome. Thus, the internal friction of liquids, like that of solids, is of an energetic nature. The higher the energy of intermolecular interaction, the greater the internal friction of the liquid.

If a liquid flowing through a narrow tube is divided arbitrarily into concentric layers, it will be found that these layers move at different velocities. The velocity of the liquid layer adjacent to the tube wall is zero (i.e., this layer is immobile), whereas the liquid layer in the middle part is moving at the highest velocity. Thus, in a direction perpendicular to that of the movement of the liquid there is a certain *gradient of velocity* (du/dz). In the general case the velocity gradient is variable. To keep the velocity distribution constant an external force has to be applied, equal in magnitude but opposite in sign to the internal friction f. The force that must be applied is related to the gradient of velocity du/dz by the following equation (Newton's law):

$$-f = F = \eta S \frac{du}{dz} \tag{7.9}$$

where S = area of contact between liquid layers
η = proportionality factor known as the coefficient of viscosity, or simply viscosity.

Rate of flow is the speed of development of an irrecoverable shear deformation D, i.e.,

$$u = \frac{dD}{dt} \tag{7.10}$$

Hence,

$$\frac{du}{dz} = \frac{d^2D}{dz\,dt} \tag{7.11}$$

The quantity $\frac{dD}{dz}$ is the relative shear γ and hence,

$$\frac{du}{dz} = \frac{d\gamma}{dt} \tag{7.12}$$

Combining Eqs. (7.12) and (7.9) and the relation $\sigma_{sh} = F/S$, Newton's law can be written in the following form:

$$\sigma_{sh} = \eta_{sh} \frac{d\gamma}{dt} \tag{7.13}$$

Hence, the shear stress is directly proportional to the rate of relative shear.

7.3. ELASTOVISCOUS AND VISCO-ELASTIC BODIES

Up till now we have been discussing ideal cases of deformation — elastic strain of solids, which obeys Hooke's law, and flow of a liquid, which obeys Newton's law. There are two simple types of deviation of the behaviour of real bodies from ideal deformation:

1. Absence of direct proportionality between strain (in a solid) or rate of deformation (in a liquid) and stress, i.e., nonconformity with Hooke's and Newton's laws.

2. Simultaneous dependence of stresses on strain deformation and on rate of deformation, as well as on higher derivatives of deformation with respect to time. Such anomalies are characteristic of systems combining the properties of solids and liquids. Bodies in which they are observed are called *visco-elastic* or *elastoviscous.**

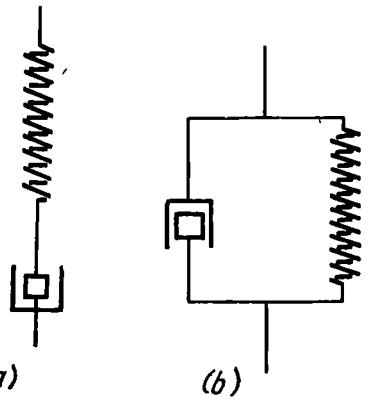

Fig. 7.2. Maxwell (*a*) and Kelvin (*b*) models

In a number of cases the experimental strain-to-stress ratios are functions of time only $[\sigma/\varepsilon = f(t)]$ but not of stress or strain. Such cases are said to conform with the relations of the linear visco-elastic theory.

The first model simulating the behaviour of an elastoviscous body, suggested by Maxwell, consisted of a spring (elastic deformation) and a dashpot moving in a viscous medium (irrecoverable flow deformation), the two elements being connected in series (Fig. 7.2*a*). Kelvin, and later Voigt, simulated the behaviour of a

* In the Soviet literature the term *elastoviscous* is used to denote fluid bodies possessing elasticity (rubber-like liquid polymers and their solutions). *Visco-elastic* bodies are elastic nonfluid bodies possessing internal friction (spatially cured polymers, gels, etc.).

visco-elastic body by means of a spring and dashpot combined in parallel (7.2*b*).

In the Maxwell model, constant stress at a given constant rate of extension is established not immediately, like in a viscous liquid, but gradually.

Maxwell showed that the rate of change of a stress in his model can be expressed by the laws:

$$\frac{d\sigma_{sh}}{dt} = G_{sh}\frac{d\gamma}{dt} - \frac{\sigma_{sh}}{\tau} \tag{7.14}$$

for shear deformation, and

$$\frac{d\sigma_n}{dt} = E\frac{d\varepsilon_n}{dt} - \frac{\sigma_n}{\tau} \tag{7.15}$$

for tensile strain. In these equations:

σ_{sh} and σ_n = shear and normal stress, respectively
t = time of deformation
γ and ε_n = shear and tensile strain
G_{sh} = shear modulus
E = modulus of elasticity
τ = constant, the meaning of which will be discussed below.

At constant stress $\left(\sigma = \text{const};\ \frac{d\sigma}{dt} = 0\right)$ Eqs. (7.14) and (7.15) become

$$G_{sh}\frac{d\gamma}{dt} - \frac{\sigma_{sh}}{\tau} = 0 \quad \text{and} \quad E\frac{d\varepsilon_n}{dt} - \frac{\sigma_n}{\tau} = 0$$

whence

$$\sigma_{sh} = G_{sh}\tau\frac{d\gamma}{dt} \tag{7.16}$$

$$\sigma_n = E\tau\frac{d\varepsilon_n}{dt} \tag{7.17}$$

Comparison of Eqs. (7.16) and (7.17) with Eq. (7.13) shows that the product of the constants $G_{sh}\tau$ and $E\tau$ is equal to the coefficient of viscosity:

$$\eta_{ext} = E\tau \tag{7.18}$$

$$\eta_{sh} = G_{sh}\tau \tag{7.19}$$

It follows from Eqs. (7.18) and (7.19) that the coefficient of viscosity for extension (or compression) is not equal to that for shear. With bodies whose $\mu = 0.5$, $E = 3G_{sh}$ (p. 179) and $\eta_{ext} = 3\eta_{sh}$, i.e., the coefficient of viscosity measured for tensile strain is three times as large as that measured for shear strain.

At constant strain $\left(\varepsilon = \text{const};\ \frac{d\varepsilon}{dt} = 0\right)$ Eqs. (7.14) and (7.15) for an elastoviscous body have the form

$$\frac{d\sigma_{sh}}{dt} = -\frac{\sigma_{sh}}{\tau} \quad \& \quad \frac{d\sigma_n}{dt} = -\frac{\sigma_n}{\tau} \tag{7.20}$$

or both cases may be written as

$$\frac{d\sigma}{\sigma} = -\frac{dt}{\tau} \tag{7.21}$$

Integration of Eq. (7.21) gives

$$\ln\frac{\sigma}{\sigma_0} = -\frac{t}{\tau}$$

or

$$\sigma = \sigma_0 e^{-t/\tau} \tag{7.22}$$

where σ_0 = initial stress at $t = 0$, characterizing the nonequilibrium state of the body
σ = stress after a certain interval of time t.

It follows from Eq. (7.22) that $\sigma < \sigma_0$, i.e., the stress in the specimen decreases with time, vanishing theoretically after a very long time interval t. However, largely the change in stress occurs over a definite interval of time, and it follows from Eq. (7.22) that if the stress decreases e times (e being the base of Napierian logarithms) during a certain length of time t, i.e., $\sigma = \frac{1}{e}\sigma_0$ then

$$\tau = t \tag{7.23}$$

Hence, the constant τ has the dimension of time. The value τ is the time needed for the stress in a specimen to decrease by a factor of e and is often called the *relaxation time* (p. 190).

In the Kelvin model the stresses in the σ_{el} and σ_{visc} branches add up, and the total stress σ is equal to

$$\sigma = E\varepsilon + \eta\frac{d\varepsilon}{dt} \tag{7.24}$$

where E = modulus of elasticity
η = coefficient of viscosity
ε = relative strain
$d\varepsilon/dt$ = rate of change of relative strain with time.

At $\sigma = \text{const}$

$$\varepsilon = \frac{\sigma}{E} + Ce^{-\frac{E}{\eta}t} \tag{7.25}$$

where C is the integration constant, equal to $-\sigma/E$.

It follows from Eq. (7.25) that at a very large time t the strain reaches the constant value $\varepsilon = \sigma/E$.

If a body is deformed to $\varepsilon = \varepsilon_0$ and then the stress is released, the strain will decrease gradually until it vanishes completely. Hence, with $\sigma = 0$

$$\varepsilon = \varepsilon_0 e^{-\frac{E}{\eta}t} \tag{7.26}$$

The quantity $\eta/E = \tau_r$ determining the rate of decrease of the strain is called the *retardation time.*

7.4. RUBBER-LIKE DEFORMATION

7.4.1. Rubber-Like Elasticity of an Ideal Rubber

We shall examine rubber-like behaviour using the so-called *ideal rubber model*, which is a body capable of deforming greatly without changing its volume when small stresses are applied.

Figure 7.3 is a typical stress-strain curve for simple extension of an ideal rubber.

It can be seen that Hooke's law is observed only for small strains, i.e., in the first section of the curve. In the second section minor changes of stress cause large strains (rubber-like deformation). The third section corresponds to a sharp increase in stress with insignificant changes in strain, this being due to a change in the structure of the material. In the second section the modulus of elasticity is not constant, its value varying with stress. However, for practically all stresses the elasticity modulus of rubber is small, being equal approximately to 0.02 kgf/mm², i.e., is of the same order as that of gases (see p. 181).

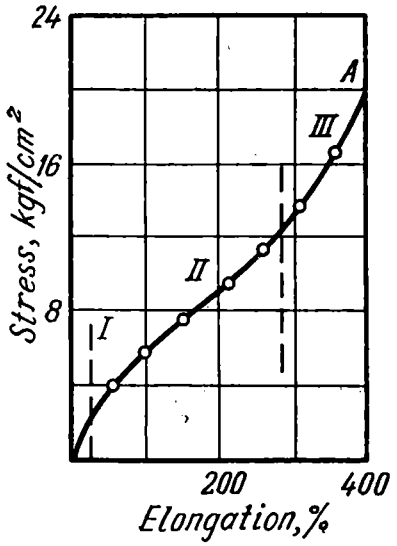

Fig. 7.3. Typical stress-strain curves for a rubber-like polymer

This suggests that rubber-like elasticity of polymers is *kinetic by its nature.* This seems all the more likely since the elasticity modulus of rubber, like that of gases, increases with temperature and deformation increases the temperature of elastic bodies. On the other hand, constancy of volume at small strains is evidence that the mean distances between the rubber molecules do not change, that is, the internal energy remains constant.

The kinetic nature of the elasticity of a gas is due to the mobility of its molecules. The giant molecules of a polymer have little mobility at ordinary temperatures, and therefore rubber-like deformation cannot be determined by the mobility of the entire chain.

It is due to the thermal motion of the chain units, which accounts for the flexibility of long chains.

The equilibrium state of a flexible chain is its coiled form (Chap. 4). If such chains are extended by external forces, the thermal motion of the chain units will act counter to the external forces. But this counteraction is not great, and chains straighten out under comparatively small stresses (their conformation changes), which may be accompanied by a very great elongation of the specimen. After the load is removed the chains return to their initial state, i.e., coil up, and the specimen recovers its initial length; hence, rubber-like deformation is recoverable.

Thus, from the molecular point of view rubber-like elasticity consists essentially in straightening of coiled long flexible chains under an applied load and in recovery of their initial shape after the load is removed. In the ideal case only small chain sections are displaced, but the chain as a whole does not move perceptibly (absence of flow).

Now let us consider the thermodynamics of rubber-like behaviour. In a reversible process occurring at constant volume and constant temperature the change of free energy is related to the change of internal energy and entropy by the expression:

$$dF = dU - T\,dS \tag{7.27}$$

On the other hand, $dF = \delta A$, where A is the useful work done on the system. If it is tensile work, then $\delta A = f\,dl$, where f is the force and dl is the change in length of the specimen. Hence,

$$f\,dl = dU - T\,dS \tag{7.28}$$

or

$$f = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T \tag{7.29}$$

It follows from Eq. (7.29) that there may be two types of elastic forces, one associated with the change in internal energy, and the other, with the change in entropy and with thermal motion.

On deformation of an ideal crystal the changes in relative arrangement of its ions or atoms are very small and may be neglected, and therefore the term $(\partial S/\partial l)_T = 0$. Hence,

$$f = \left(\frac{\partial U}{\partial l}\right)_T \tag{7.30}$$

i.e., the work done by the external straining force goes only to change the internal energy. The deformation of an ideal crystal is purely energetic in nature.

Deformation of ideal rubber involves no change in internal energy and hence $(\partial U/\partial l)_T = 0$. Therefore the elastic forces are

due only to the second term of Eq. (7.29):

$$f = -T\left(\frac{\partial S}{\partial l}\right)_T \tag{7.31}$$

Thus, the deformation of ideal rubber depends on temperature and on the change of entropy, which is an indication of the kinetic nature of this phenomenon.

We have examined the essentials of rubber-like deformation from the molecular and the thermodynamic standpoint. A third approach possible in examining any phenomenon is the statistic approach, which gives an insight into the interrelation between macroscopic and thermodynamic quantities and molecular behaviour. This relation is given by Boltzmann's law:

$$S = k \ln W \tag{7.32}$$

where S = entropy of the system
W = thermodynamic probability
k = Boltzmann constant.

Eq. (7.32) is used in the statistical theory of rubber-like elasticity in which the basic polymer is regarded as a rare ideal molecular network. In such a network, the chain being deformed is the section of a molecule between crosslink points, i.e., between two adjacent crosslinks, the molecular mass of this section is denoted by M_n (the assumption of a network is necessary in order to exclude flow processes). In addition, it is taken that the units of a chain freely rotate, i.e., the sections between crosslink points are very flexible and easily straighten out upon deformation, being accompanied with a decrease in the number of possible conformations, i.e., a decrease in thermodynamic probability and entropy. The authors of the theory have obtained the following expression for stress and the Young modulus by using the expression for thermodynamic probability (p. 101) and calculating the change in entropy upon deformation:

$$\sigma = \frac{d \cdot RT}{M_n}\left(\lambda - \frac{1}{\lambda^2}\right) \tag{7.33}$$

$$E = \frac{3RTd}{M_n} \tag{7.34}$$

where d = polymer density, g/cm^3

$\lambda = \frac{l}{l_0}$ = relative elongation, or degree of extension.

Linear dependence of the elasticity modulus on the absolute temperature is confirmed by experiment, but owing to the basic assumptions (free rotation of units, disregard of the change in internal energy upon deformation and of intermolecular interaction) the behaviour of real rubber-like materials does not correspond to the theory of rubber-like elasticity.

7.4.2. Rubber-Like Elasticity of a Real Rubber

Laws governing rubber-like deformation of real rubbers are much more complex than for an ideal rubber.

1. Deformation of real rubbers involves a change in volume, i.e., $V \neq \text{const}$. This means that the mean distance between chains changes, and consequently the energy of interaction also changes. In other words, the deformation of real rubbers involves not only a change of entropy but of internal energy as well. Hence, rubber-like deformation has not only a kinetic, but also an energetic nature.

This was theoretically shown first by Volkenshtein and Ptitsyn, and later by Flory and his coworkers. Recent experimental works have revealed that the elastic force which originates in the deformation process is not a "purely entropy" force, but includes also a change in internal energy. The energy component of an elastic force in some cases constitutes one-half of the overall straightening force or even more. Plate, Shibaev and their coworkers have shown that the elastic properties of polyalkylacrylates are well described by the equations of the statistical theory of elasticity, and the elastic force which originates in the process of their elongation is mainly set by a change in entropy. In contrast to this, polyalkyl methacrylates are deformed with an increase in entropy and a considerable change in internal energy, whose contribution depends on the degree of elongation. The elastic properties of the latter do not comply with Eq. (7.33); they are described by the empirical Mooney-Rivlin equation

$$\sigma = (C_1 + C_2\lambda^{-1})(\lambda - \lambda^{-2}) \qquad (7.35)$$

where $\lambda = \frac{l}{l_0}$ and C_1 and $C_2 =$ constants for a given polymer.

Such a difference in the behaviour of polymers is apparently due to the fact that intermolecular interaction is greater in the polymethacrylate series than in polyacrylates.

2. Rubber-like deformation may be observed only in a certain range of stresses and deformations. Maximum orientation of macromolecules occurs at higher stresses and degrees of deformation (region *III* on the curves in Fig. 7.3); for polymers which are being crystallized, this orientation leads to their crystallization (p. 245). In this case, the nature of deformation qualitatively changes; it becomes only energetic, i.e., under the influence of the external field, there are deviations of the atoms of the molecular chain from their equilibrium positions, like in ordinary crystals.

On deformation of noncrystallizable rubbers their flexible chains straighten out to such an extent at large elongations that they behave like rigid formations. Thus, in cases where chain flexibility

decreases, the nature of the deformation changes and the modulus of elasticity increases sharply.

3. The deformation of a real rubber is never purely rubber-like. Straightening of chains and the change in their shape is accompanied by relative displacement of the chains, i.e., by flow, which results in permanent set. Therefore, the total change in chain length upon extension or compression of a rubber sample is always the result of both rubber-like strain and flow deformation.

There is a number of methods of separating them (see p. 201).

To avoid or minimize flow, rubber-like deformation is studied at such low temperatures (but above T_g), that the movement of the chain as a whole can be neglected, or a network of low crosslink density is set up in the polymer. With a low concentration of crosslinks mutual displacement of the chains is impossible, but the crosslinks are sufficiently long to display chain flexibility.

4. An important feature of the behaviour of real rubbers is related to the nonequilibrium nature of rubber-like deformation, to its *relaxational* nature.

7.5. RELAXATION PROCESSES

The term *relaxation* is usually used to denote the process of establishment of statistic equilibrium in a physical or physicochemical system. The rate of establishment of equilibrium is related to the probability of transition of the system from one state of equilibrium to another. These transitions may be due to various causes. Thus, in a liquid, continuous regrouping of molecular clusters occurs under the influence of thermal motion; the probability of this process is expressed by Boltzmann's law:

$$W = \nu_0 e^{-\Delta U/RT} \tag{7.36}$$

where ν_0 = intrinsic frequency of molecular vibration, which is almost the same in a liquid as in a solid ($\nu_0 = 10^{13}$-10^{14} vibrations/sec)

ΔU = activation energy, i.e., difference in the energies of the active (intermediate) and initial states of the molecules.

The reciprocal of the probability of regroupings characterizes their rate and is known as the *relaxation time* of the process:

$$\tau = \tau_0 e^{\Delta U/RT} \tag{7.37}$$

where τ_0 is the period of vibration of atoms, equal to ca. 10^{-13} sec.

The smaller the value of ΔU and the higher the temperature, the smaller the relaxation time. At temperatures above the crystallization temperature, the relaxation time of low-molecular liquids is low, ca. 10^{-10} sec. This is the lifetime of an ordered group of molecules: in the course of this time interval any given ordered region

may break down and another ordered region may form. Small relaxation times are the reason for the rapid establishment of equilibrium states in low-molecular liquids.

As was indicated above, a specific feature of polymer structure is that a polymer contains two kinds of structural elements, namely, chain units and the chains themselves. These elements differ considerably in size, and hence in mobility.

Units are of the same order of size as molecules of low-molecular substances. If the units were not linked into a chain, their mobility due to thermal motion would be the same as that of the molecules of low-molecular liquids. But since the units are chemically bound into very long chains, their mobility is greatly constricted. However, the mobility of units in the rubber-like state is still sufficiently high for them to regroup at perceptible rates. The time necessary for such regroupings, i.e., the relaxation time of units, is 10^{-4}-10^{-6} sec, which is 4-6 orders greater than the relaxation times of low-molecular liquids.

Owing to their large sizes, polymer chains possess low mobility and their relaxation times are very high. For this reason a change in temperature of a polymer in the rubber-like state mainly causes regrouping of its units, i.e., a change of chain conformation.

Processes in which equilibrium is established in time are called *relaxation processes*. They include equalizing of nonuniformly distributed concentration of a solute by diffusion, orientation of dielectric molecules in an electric field, or return of oriented dipoles to random arrangement after removal of the external electric field (Chap. 11), and the development of rubber-like strain.

Relaxation times are judged by the rate at which the macroscopic quantities characterizing the state of a system asymptotically approach their equilibrium values. If the deviations from equilibrium are small, these quantities change according to the law

$$y = y_0 e^{-t/\tau} \tag{7.38}$$

where y_0 = value of the property y at $t = 0$
t = time elapsed from the initial moment
τ = relaxation time.

Eq. (7.38) is an analogue of Eq. (7.22) in which τ is relaxation time.

7.5.1. Relaxation Nature of Rubber-Like Elasticity. Equivalence of Time and Temperature

The relaxation nature of rubber-like deformation was first disclosed by Kobeko, Aleksandrov, and Lazurkin, who demonstrated the relation between the temporal nature of change in size of an elastic polymer sample and its structural features.

Rate of Development of Rubber-Like Deformation. Suppose a constant stress much smaller than the breaking stress (Chap. 9) is applied to a polymer sample. If this does not cause flow, the sample will become gradually longer under the action of the applied stress, until it reaches a definite length which changes no longer with time. The strain per unit length that changes no longer with time is called the *equilibrium rubber-like strain* and is denoted by $\varepsilon_{el,\infty}$. The equilibrium strain is always larger than any strain developed during a given time interval $t(\varepsilon_{el,\infty} > \varepsilon_{el,t})$.

To each stress value there corresponds a definite equilibrium strain. These quantities are related by an expression similar to Hooke's law:

$$\sigma = E_\infty \varepsilon_{el,\infty} \tag{7.39}$$

where E_∞ is the equilibrium modulus of elasticity.

Until the value $\varepsilon_{el,\infty}$ is reached the sample is in a nonequilibrium state.

The strain developed in a given time interval is related to the stress by the equation:

$$\sigma = E_t \varepsilon_{el,t} \tag{7.40}$$

where E_t is a modulus characterizing the strain developing in a given time interval t.

Since $\varepsilon_{el,t} < \varepsilon_{el,\infty}$, $E_t > E_\infty$.

After the stress is removed the strain also changes in time as the sample recovers its initial shape. Similar phenomena are observed during compression.

If there is no flow, i.e., the deformation is purely rubber-like, the sample will recover its dimensions completely, but this may require a very long time. Thus, rubber-like deformation depends not only on the magnitude of stress applied, but also on the loading time.

Stress Relaxation. Let us subject a polymer sample to very rapid (theoretically instantaneous) strain and fix it in the deformed state. Obviously, equilibrium strain will not have time to develop at such short notice. The stress arising in the sample is $E_t \varepsilon_{el,t}$. Since the modulus E_t is many times larger than the equilibrium modulus E_∞, the stress will also be very great. After some time a rubber-like strain corresponding to a low modulus will develop as a result of regrouping of the units, thus decreasing the stress in the sample.

This process is called *stress relaxation*, and the time during which the stress in the sample decreases by e times is known as the *relaxation time* (see p. 185).

Figure 7.4 shows typical stress relaxation curves of amorphous polymers. It is evident from the figure that the higher the tem-

perature, the faster will the stress in the sample decrease. By measuring the stress in the sample at a given elongation one can calculate a modulus, called the *modulus of relaxation* (or *stress-relaxation modulus*). The time of measurement may be standardized at, say, 10 s. Then the measured value of the stress-relaxation modulus is denoted as E_{10}.

The strain developing in a given time interval is calculated by the Kelvin equation [Eq. (7.25)], under the assumption that the

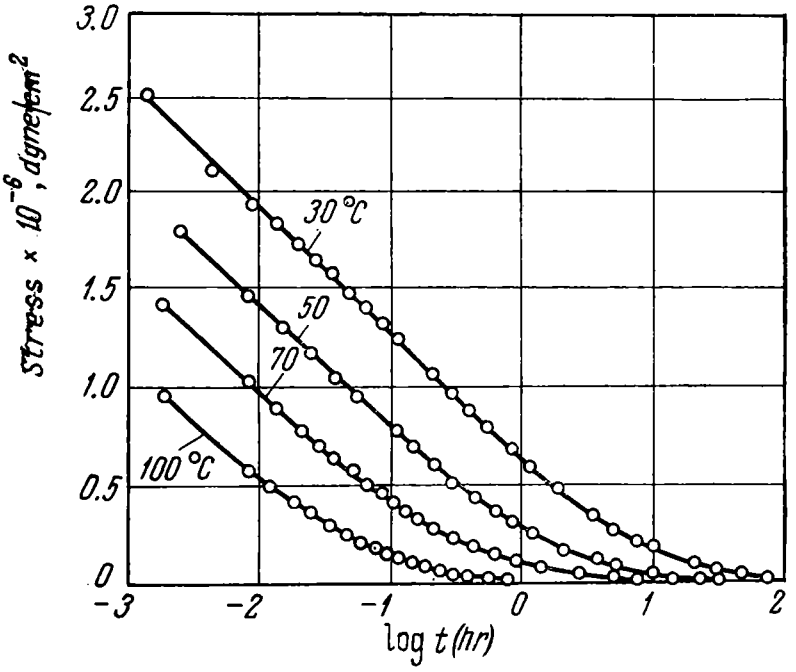

Fig. 7.4. Stress relaxation curves in the viscoelastic region for infractionated polyisobutylene (mol. mass 1 340 000) at 50 per cent elongation

relaxing material behaves like a simple visco-elastic body and the strain gradually reaches its equilibrium value $\varepsilon_{el,\infty} = \sigma/E$. Then the Kelvin equation becomes:

$$\varepsilon_{el,t} = \varepsilon_{el,\infty}\left(1 - e^{-t/\tau_r}\right) \tag{7.41}$$

where $\varepsilon_{el,\infty}$ = equilibrium value of rubber-like strain
t = deformation time
τ_r = retardation time.

The strain develops gradually because under the action of the forces applied the changes in chain conformation acquire a definite direction and require time. This time (retardation time) can be expressed by Eq. (7.36), the quantity ΔU being the difference in the energies of the active and initial states for the process of rubber-like deformation, or the *activation energy of rubber-like deformation*, as it is called.

In the general case the strain per unit length of a polymer ε_{tot} is composed of elastic strain ε_{el} (determined by the change in distances between atoms in the chain), rubber-like strain $\varepsilon_{el,\,t}$ and flow deformation ε_{fl}

$$\varepsilon_{tot} = \varepsilon_{el} + \varepsilon_{el,\,t} + \varepsilon_{fl}$$

At fairly low temperatures the relaxation time of the chains becomes so large that the flow deformation may be neglected. Then

$$\varepsilon_{tot} = \varepsilon_{el} + \varepsilon_{el,\,t} \tag{7.42}$$

Substituting Eqs. (7.37) and (7.41) into Eq. (7.42) one obtains

$$\varepsilon_{tot} = \varepsilon_{el} + \varepsilon_{el,\,\infty}\left(1 - e^{-\frac{t}{\tau_0 e^{\Delta U/kT}}}\right) \tag{7.43}$$

Assuming ε_{el}, τ_0, and ΔU to be constant, one can calculate ε_{tot} values for various times and temperatures. The calculation shows that strain develops gradually, and the higher the temperature, the sooner it reaches its equilibrium value (Fig. 7.5). This conclusion is in good agreement with the experimental data given in Fig. 7.6.

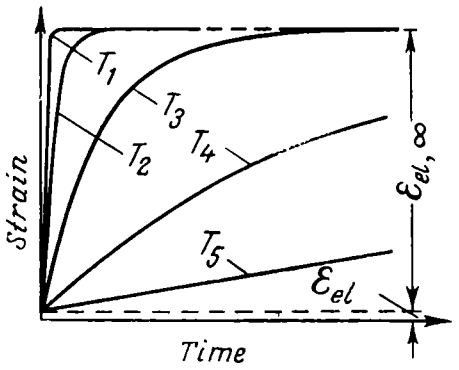

Fig. 7.5. Time dependence of strain of polymers at various temperatures ($T_1 > T_2 > T_3 > T_4 > T_5$)

Figure 7.6 is the time dependence of the strain of soft rubber vulcanizates at different temperatures. The upper line corresponds to the equilibrium strain, which develops practically instantaneously in the temperature interval between 7 and 60 °C. With decreasing temperature the time required to reach equilibrium strain increases; at —70 °C equilibrium strain is practically not reached at all. It follows from Fig. 7.6 that in the temperature range where the polymer displays rubber-like properties the equilibrium highly elastic strain is almost independent of temperature; temperature only affects the rate of attainment of equilibrium.

This conclusion follows from Eq. (7.39), according to which the relaxation time decreases with rising temperature, i.e., regrouping of units occurs faster owing to the increase in intensity of thermal motion. Thus, a change of temperature should affect the rate of relaxation processes.

On the basis of the theoretical curves deformation vs. temperature curves can be plotted for a constant stress acting over various time intervals (t_1, t_2, t_3, ...). This dependence is shown in Fig. 7.7.

It follows from the figure that at low temperatures the deformation is very small and practically independent of the time of force action. At these temperatures the relaxation time is much greater

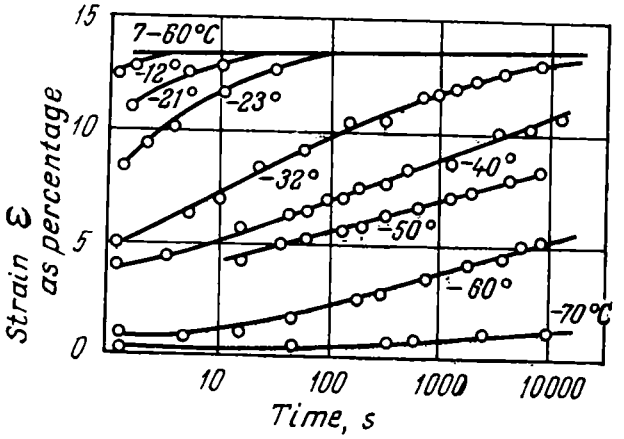

Fig. 7.6. Time dependence of highly elastic strain of rubber. The numbers of the curves give the temperature in degrees C

than the time of deformation ($\tau \gg t$); therefore practically any time interval, no matter how long, would be insufficient for the units to rearrange themselves. At high temperatures, on the

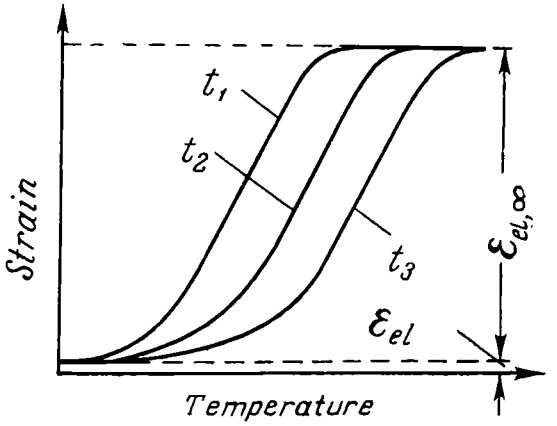

Fig. 7.7. Temperature dependence of strain of polymers for various deformation times ($t_1 > t_2 > t_3$)

contrary, the relaxation time of the unit is very small ($\tau \ll t$) and rubber-like deformation can develop irrespective of the loading time; therefore the deformation is also independent of the time of loading.

But for any polymeric material there is a temperature range, within which the relaxation time and time of deformation are commensurable. Within this intermediate temperature range the deformation is sharply dependent on the time of loading t. If it is

greater than the relaxation time τ, deformation will be able to develop. If t is smaller than τ, no rubber-like deformation will be able to develop. For instance, at a certain temperature T_1 and

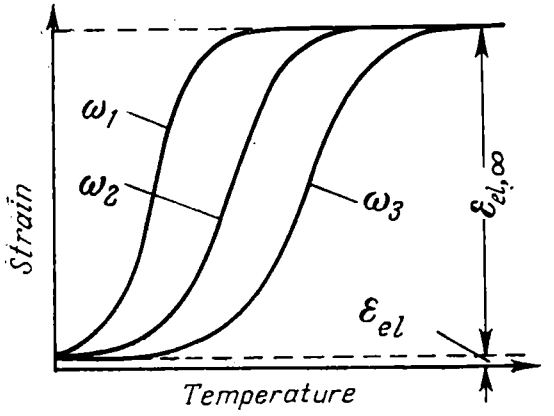

Fig. 7.8. Temperature dependence of deformation of polymers at various loading frequencies ($\omega_1 < \omega_2 < \omega_3$)

loading time t_1 the deformation developed in the material will be close to its equilibrium value, but at the same temperature and loading time $t_3 < t_1$ the deformation may be very small and the

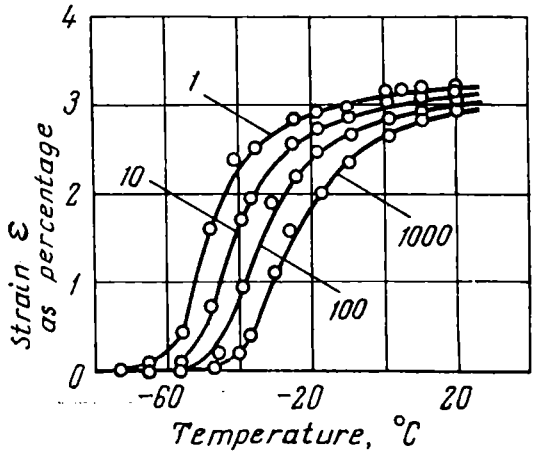

Fig. 7.9. Temperature versus compressive strain for natural rubber. The numbers on the curves give loading frequency in Hz

material will behave like an elastic, rigid substance rather than like a rubber-like one (see Fig. 7.7).

Thus, the idea of rubber-like deformation as of a relaxation process is based on the fact that the deformation depends on the ratio between the relaxation time and the time of deformation.

Figure 7.8 gives the theoretical curves of ε vs. T at various frequencies of loading, and Fig. 7.9, experimental curves obtained on the instrument designed by Aleksandrov and Gayev. It follows

from these figures that at $T = \text{const}$ the deformation values of a sample are much larger on slow (low frequencies) than on fast deformation. The same deformation can be obtained by changing either frequency or temperature; hence, all the experimental data given are evidence of the equivalence of temperature and time of loading.

7.5.2. Calculation of Relaxation Time and Activation Energy of Rubber-Like Deformation. Spectrum of Relaxation Times

Since rubber-like deformation develops in time at a certain rate, the value in the exponent of Eq. (7.40) is the activation energy of the process, being known as the *activation energy of rubber-like deformation*. The values of ΔU and τ may be calculated for different temperatures. Theoretically, the point which conforms to $\varepsilon = \frac{\varepsilon_\infty}{2}$ on the curves in Fig. 7.8 corresponds to $\omega\tau = \sqrt{3}$. Hence, the value of τ may be calculated on the basis of certain values of frequencies. Figure 7.10 shows the dependence of the values of relaxation times τ, which have been calculated by this method, on temperature for some polymer materials. The values of τ change within the range of 10^{-3}-10^{+2} s as temperature drops.

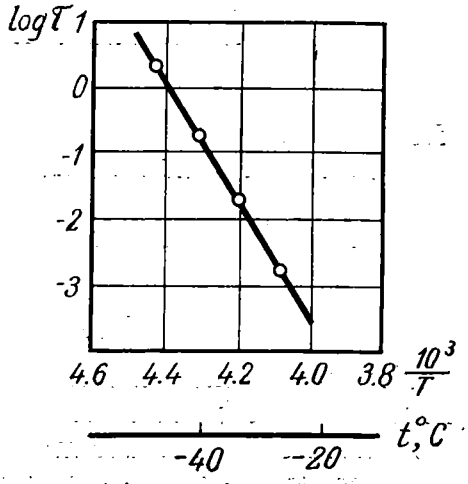

Fig. 7.10. Dependence of the relaxation time of highly elastic deformation on inverse temperature

Taking the logarithm of Eq. (7.37), we obtained

$$\log \tau = \log \tau_0 + \frac{\Delta U}{2.303R} \cdot \frac{1}{T} \quad (7.44)$$

In the given temperature range (Fig. 7.10), the dependence $\log \tau = f\left(\frac{1}{T}\right)$ is rectilinear. Hence, the value of ΔU may be calculated from the slope of straight lines.

This dependence is curvilinear in a wider temperature range; as Lazurkin indicates, Eq. (7.44) may be used to calculate ΔU, taking $\tau_0 \cong 10^{-12}$ s, i.e., a value which is close to atomic vibration time (p. 206). The activation energy of rubber-like elasticity for natural rubber that has been found in this way depends on temperature: when the latter increases from —50 to —20 °C, ΔU decreases from 59 kJ/mole to 46 kJ/mole.

Relaxation time which is determined from the empirical curves according to the aforementioned method should be regarded as

average relaxation time, since real polymers have a wide set or *spectrum* of relaxation times that conform to the regroupings of chain units and chain regions, which consist of a different number of units, and also the regroupings of larger supermolecular structures.

A characteristic feature of relaxation of polymers is that it involves a large number of simultaneous processes proceeding at different rates, i.e., at different relaxation times.

This issues from a detailed analysis of an experiment. Thus, it follows from Fig. 7.9 that the frequency dependence of deformation remains at sufficiently high temperatures, though it should be absent in a system with one relaxation time (Fig. 7.8). For spatially crosslinked polymers at elevated temperatures, equilibrium rubber-like deformation is not observed at any frequency, i.e., deformation continues to lag behind stress. Other experimental data which testify to the presence of a spectrum of relaxation times are available, and there are methods for estimating them.

7.5.3. Time-Temperature Superposition. Ferry's Reduction Method

It follows from the previous section that to obtain information on the viscoelastic properties of polymeric systems measurements have to be made over a wide range of the time scale, covering many orders of magnitude. When measuring stress relaxation one usually varies the time intervals from 10 to 10^6 s (ca. 10 days). (In the studies by A. P. Aleksandrov and Yu. S. Lazurkin the time was varied over four decimal orders.) But even such time intervals do not cover the entire set of relaxation properties. For this reason it was very important to find a method of extrapolation which would make it possible to pass from one time of loading to another. Such an extrapolation equation, first derived by Aleksandrov and Lazurkin, was based on the principle of equivalence of temperature and time:

$$\log t_0 - \log t = \beta\left(\frac{10^3}{T_0} - \frac{10^3}{T}\right) \qquad (7.45)$$

where t_0 and t = times of loading
T_0 and T = temperatures at which the strain value decreases in half on cooling
β = constant.

The law of equivalence, confirmed subsequently by a large amount of experimental material in the works of Leaderman, Tobolsky, Ferry, and others, has become known as the *time-temperature superposition principle*.

Analyzing the data of Kobeko, Kuvshinsky, and Gurevich (see Fig. 7.6), Leaderman showed that the deformation curves could be superimposed by shifting them along the logarithmic time axis. This means that the effect of temperature on relaxation properties is equivalent to multiplication (or division) of the time scale by a definite coefficient for each temperature. Such superposition of curves is possible for any relaxation processes in the linear viscoelastic region (p. 183).

The time-temperature superposition principle was used extensively by Tobolsky, who obtained experimental data at different temperatures and practically convenient times. Transition to a single convenient reference temperature and a wide range of times is based on the fact that with increasing temperature the time of the experiment decreases, i.e., the principle of equivalent effect of time and temperature comes into action. Ferry and coworkers showed that the temperature dependence of all mechanical and electrical properties of amorphous polymers above their glass transition temperatures can be described by a single empirical function a_T, which is the ratio of relaxation times at temperature T and a reference temperature T_0, and is known as the *shift factor*:

$$a_T = \frac{\tau_T}{\tau_{T_0}} \tag{7.46}$$

The value of a_T reflects primarily the temperature dependence of the friction coefficient of the chain segments on which the rate of conformation rearrangement depends.

Very important in Ferry's method is the choice of reference temperature T_0. This temperature should be the same as far as possible for different systems. Room temperature would be very convenient. However, with room temperature as the reference point all the curves intersect at $T = T_0$, but differ greatly in nature.

It has been found that a reference temperature T_s can be selected for each system, and a_T can be expressed as a function of the difference $T - T_s$ so that this function is identical for many polymers as well as for their solutions. The best temperature would be the glass transition temperature of each polymer, but this brings up a number of difficulties because its position is affected by small amounts of residual solvents, thermal history, and other factors. Besides, viscosity and other mechanical properties are very difficult to measure near T_g, and there is practically no data for this range of temperatures. For this reason Williams suggested using as the reference temperature a temperature $50 \pm 4°$ above the T_g of any polymer.

Thus,

$$a_T = \frac{\eta T_s \rho_s}{\eta_s T \rho} \tag{7.47}$$

where η and ρ = viscosity coefficient and density of polymer at temperature T

η_s and ρ_s = same values at reference temperature T_s.

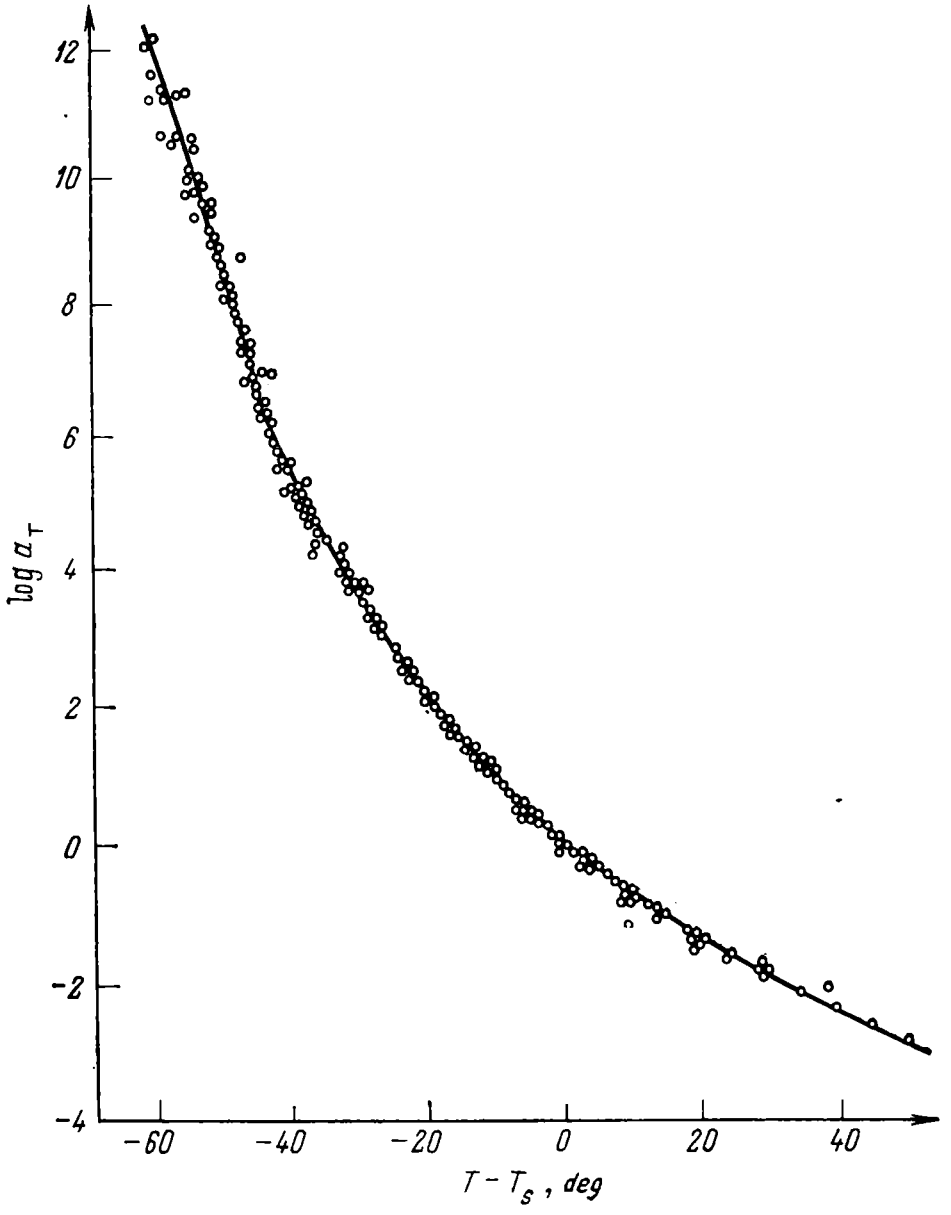

Fig. 7.11. Log a_T vs. $T - T_s$ for various polymeric systems

Table 7.2 lists the reference temperatures for several polymers. If a reference temperature $T_s = 243$ °K is selected for polyisobutylene, the $\log a_T$ vs. temperature curve for the other polymers can be found by shifting their curves along the x and y axes (using tracing paper) until they coincide with the curve for polyisobuty-

TABLE 7.2 *Reference Temperature T_s for Various Polymers*

Polymer	T_s, °K	$T_s - T_g$
Polyisobutylene	243	41
Polystyrene	408-418	35-45
Poly(vinyl acetate)	349-351	44-46
Poly(methyl methacrylate)	341-435	53-57
Poly(vinyl chloride)	393-396	46-49
Natural rubber (unvulcanized)	247-251	47-51

lene. Such shifts result in a master curve for all polymers shown in Fig. 7.11, which can be expressed by the equation:

$$\log a_T = -C_1 \frac{T - T_s}{C_2 + (T - T_s)} \tag{7.48}$$

where C_1 and C_2 are empirical constants.

This equation is also valid for the ratio of viscosities of the polymers at temperature T and reference temperature T_s.

If T_g of the polymer is taken as the reference temperature, the values of the constants C_1 and C_2 can be calculated. In this case Eq. (7.48) becomes

$$\log a_T = \log \frac{\eta(T)}{\eta(T_g)} = -\frac{17.44\,(T - T_g)}{51.6 + (T - T_g)} \tag{7.49}$$

Equation (7.49) is called the Williams-Landel-Ferry (WLF) equation.

7.5.4. Creep of Polymeric Materials

The deformation of a real linear rubber-like polymer is usually a superposition of rubber-like deformation and irrecoverable flow deformation, both of these developing in time. The gradual development of a deformation is known as *creep*. The total value of a creep gives no grounds to judge of its cause. But under certain conditions the total strain can be separated into its recoverable and irrecoverable parts. This is usually done by two methods.

The first, more correct method consists in allowing the strained sample to relax fully after removal of the load under conditions ensuring the highest rate of relaxation, e.g., at elevated temperatures. This removes the recoverable changes that have taken place in the sample, and hence the residual deformation is the result only of flow. For example, if a polyisobutylene sample is strained by extension at 15 °C for 46 days, the total elongation per unit length will be 1000 per cent. The residual elongation per unit

length after relaxation is 500 per cent. This means that the polyisobutylene sample is deformed five-fold at room temperature only as a result of flow. Thus, linear polymers in the rubber-like state are capable of large irrecoverable strains. Proof of the separation of flow deformation and rubber-like strain is recovery of the initial structure of the material (the chains must acquire their initial conformations). If the structure of the material in the initial state

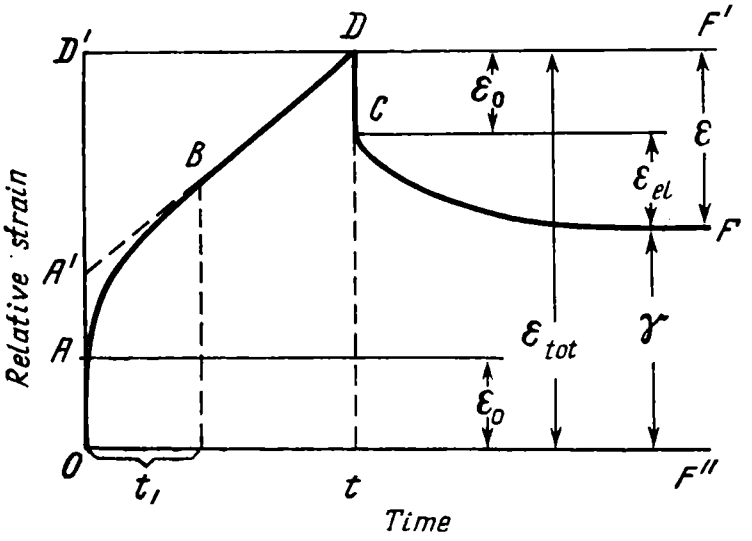

Fig. 7.12. Relative strain versus time (creep curve)

and after relaxation in the same, but the shape of the sample is different, the residual deformation observed is irrecoverable.

It should be noted that heating can be used to speed up relaxation only if it causes no chemical transformations (degradation or crosslinking) in the polymer in question.

The second way of separating irrecoverable and recoverable deformations involves measuring the strain of the polymer in time.

The time dependence of the total strain of a linear polymer at a constant stress σ_T is represented by the creep curve shown in Fig. 7.12. On this curve the section *OABD* corresponds to the change in strain on loading, and the section *DCF*, on unloading. It is evident from the figure that after application of the stress the strain develops instantaneously up to *OA*, after which it continues to increase in time along a convex (to the abscissa axis) curve *AB*, which passes into a straight line *BD*. *OA* corresponds to a small strain ε_0, which formally obeys Hooke's law and is known as the *conventionally elastic strain*. *AB* characterizes the rubber-like strain and the flow deformation developing simultaneously in time. If the rubber-like deformation has developed fully during the time interval t_1, further deformation (line *BD*) is associated only with steady flow (Chap. 10). Therefore the slope tangent of

BD characterizes the change in flow deformation per unit length in time $d\gamma/dt$. If BD is extended to its intersection with the ordinate axis, the flow deformation per unit length can be found from the triangle $A'D'D$

$$\frac{d\gamma}{dt} = \frac{\gamma}{t} = \frac{A'D'}{D'D} \quad \text{whence} \quad A'D' = \gamma$$

Thus, the intercept OA corresponds to the conventionally elastic deformation, $A'D'$, to the flow deformation, and AA', to the rubber-like deformation. OA' is recoverable and $A'D'$ irrecoverable deformation. All the above is valid only if the rubber-like strain has really reached its equilibrium value by the moment of time t_1. Otherwise the relaxing elastic strain may be mistaken for flow deformation. To avoid such a mistake it is necessary to analyze the unloading curve.

The line DC equal in length to OA, corresponds to instantaneous recovery of the elastic length of sample. Further change in length occurs gradually in time, corresponding to rubber-like strain. Finally, the sample length stops changing. The line FF'' corresponds to the permanent set due to flow. Since $FF'' = A'D'$, $A'D'$ also corresponds to the flow deformation. Substituting the slope tangent of BD into Eq. (7.13), one can calculate the viscosity coefficient:

$$\eta_{sh} = \frac{\sigma_T}{d\gamma/dt} \tag{7.50}$$

Besides, the rubber-like modulus and conventional elasticity modulus can be found from the curve in Fig. 7.12.

The conventional elasticity modulus E_1 is determined from the equation

$$E_1 = \frac{\sigma_T}{\varepsilon_0} \tag{7.51}$$

where the value of ε_0 corresponds to OA. The rubber-like elasticity modulus E_2 can be found from the equation

$$E_2 = \frac{\sigma_T}{\varepsilon_{el}} \tag{7.52}$$

where the value of ε_{el} corresponds to AA'.

7.5.5. Relation Between Rubber-Like Strain and Polymer Structure

For rubber-like strain to occur two conditions must be fulfilled: (1) the chain molecules must be sufficiently flexible, and (2) their shape must change at a sufficiently high rate, i.e., polymer chains

should possess high *kinetic* flexibility (p. 96). Such polymers are polyisoprene, polybutadiene, polyisobutylene, polychloroprene, copolymers of butadiene with nitrile of acrylic acid or with styrene that contain at least 50 per cent of butadiene (nitrile and styrene rubbers), and other rubber-like polymers, which are in a rubber-like state in a wide temperature range, including room temperature.

Rubber-like properties are not manifested in polymers with kinetically more rigid chains at ordinary temperatures; they are often in a glassy state (their mechanical properties will be considered in Chap. 9). But when they are heated above T_g, they pass over to a rubber-like state; however, they have a higher activation energy of rubber-like deformation than rubbers. For example, for polymethyl methacrylate at 130 °C it is 105 kJ/mole (25 kcal/mole). It follows that the processes of elastic deformation are more retarded.

The formation of a sparse spatial network promotes rubber-like deformation, since it prevents flow processes.

With increasing crosslink density the equilibrium rubber-like strain decreases. The formation of a large number of crosslinks results in a hard material incapable of rubber-like strain (ebonite).

7.5.6. Practical Importance of Relaxation Processes

Relaxation processes are of great practical importance, because during service many polymeric materials undergo instantaneous deformation (impact loads) or repeated deformation at high frequency. During such processes the rubber-like strain cannot attain its equilibrium value, and the material is in a nonequilibrium state. The results of static tests made with ordinary dynamometers do not reflect in such cases the service properties of the articles. Such materials should be tested under conditions close to their service conditions, i.e., at high frequencies of loading.

Relaxation processes are the essence of so-called *hysteresis* phenomena, displayed as noncoincidence of stress-strain (σ vs. ε) curves obtained by increasing the stress gradually and decreasing it gradually. Such curves are shown in Fig. 7.13, from which it is evident that the strain corresponding to the same stress value is always smaller with increasing than with decreasing stress; a loop forms between curves *1* and *2*, known as a *hysteresis loop.* After complete removal of the load the sample does not recover its initial length, i.e., a permanent set remains in it, which was originally related to flow processes. However, the presence of a hysteresis loop is not necessarily due to flow or inelastic chain

displacement. It is often a result of the relaxation nature of the developing rubber-like deformation.

In practice the cycle usually occurs so quickly that equilibrium strain does not have time to develop in the material and this equilibrium value should always be higher than that actually measured. For this reason the equilibrium deformation curve should run to the right of curve *1*. Unloading also involves relaxation, the samples recovering their size in time. Obviously, in this case the equilibrium strain values should be smaller than those actually measured, i.e., the equilibrium deformation curve for unloading should run to the left of curve *2*. If loading and unloading are carried out slowly enough to give the material time to *relax*, curves *1* and *2* will merge and there will be no hysteresis loop.

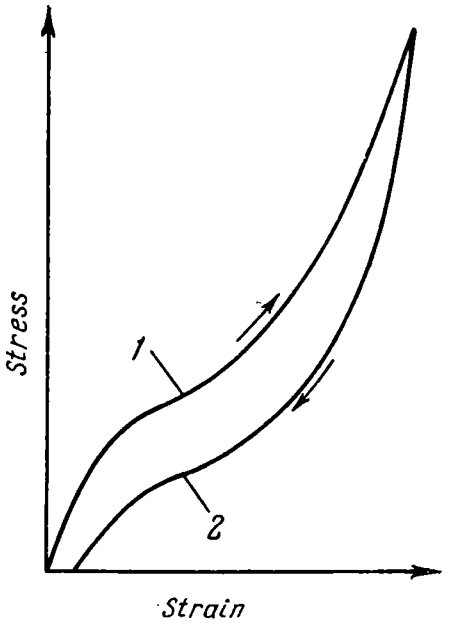

Fig. 7.13. Hysteresis loop:
1—loading; *2*—unloading.

It follows from the above that hysteresis phenomena should be interpreted with great care and that the permanent set measured after an arbitrary time from the moment of unloading should not be associated with flow processes.

Hysteresis phenomena are observed especially often when rubber articles are used at comparatively low temperatures (but above T_g), when the relaxation time is large and recovery of the size of the article after removal of the stress occurs very slowly. They play an important role at ordinary and elevated temperatures, since the area inside a hysteresis loop corresponds to a part of mechanical energy which unrecoverably passes over to thermal energy. This is known as *mechanical losses*. In the case of rapidly acting variable loads, the amount of heat liberated due to mechanical losses is very great and may cause material to become greatly heated. For example, temperature in automobile tyres may be as high as 100 °C at high speed. The heating of material is very harmful, since it leads to lower strength (Chap. 9) and chemical changes (Chap. 3). Therefore, the value of mechanical losses is an important characteristic of rubber, and it is quantitatively expressed by the tangent of the phase angle between applied sinusoidal stress and deformation. This is known as the *tangent of the mechanical loss angle*. It should be as small as possible.

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CHAPTER 8

Transition of Polymers From the Rubber-Like to the Glassy and Viscofluid States

8.1. RELAXATION NATURE OF GLASS TRANSITION

It was shown in Chapter 6 that glass transition is not a phase transition, because this process does not involve phase transformation. Glass is a nonequilibrium supercooled liquid, its structure depending to a considerable extent on the structure of the liquid melt frozen by fast cooling. In application to low-molecular glasses this has always been obvious, but the glass transition of polymers was for a long time identified with a second-order phase transition. The first to point out the erroneousness of this interpretation were Kargin and Kobeko. In this connection Kargin wrote:

"The application of the term *phase transition* to glass transition phenomena is based on purely formal analogies and lacks physical sense. Such carelessness in terminology may lead to distortion of the physical concept phase and result in major errors."

Later other authors also pointed out the erroneousness of this analogy. Flory wrote that the glassy state of a polymer is a state of "frozen disorder".

However, this disorder is rather relative, since even amorphous polymers contain organized supermolecular structures (Chaps. 5 and 6).

The transition from the glassy to the rubber-like state may involve a change in nature of supermolecular structures, but the phase state remains the same and there is no heat effect.

The difference between a glassy polymer and an elastic one is not in their phase state, but in the mobility of their macromolecules and supermolecular structures, and hence, in relaxation time, which are very large for polymers in the glassy state.

Glass transition is a typical relaxation process.

This becomes evident when studying the temperature dependence of a polymer volume.

The relaxation time of low-molecular liquids at fairly high temperatures is very small, amounting to about 10^{-10} sec. Therefore, the structure of the liquid changes practically instantaneously when the temperature is changed, and the specific volume measured at each temperature is at its equilibrium value.

When the substance is cooled, the relaxation time increases very quickly, molecular rearrangement is greatly retarded, and considerably more time is needed for the structure to reach equilibrium. On lowering of the temperature, when the substance remains at each new set of temperature conditions for a short time, its structure and volume are not at their equilibrium values and are able to change in time. Establishment of equilibrium specific volume in time is called *volume relaxation.*

A similar picture is observed when polymers pass into the glassy state. The monomer residues in the polymer chain are joined by chemical bonds and hence the total mobility of the system is much lower than that of a low-molecular liquid. However, owing to thermal motion of the units, the relaxation time in the rubber-like state is between 10^{-1} and 10^{-6} sec, i.e., relatively small. This enables elastic polymers to reach equilibrium structure at the cooling rates usually used.

The relaxation nature of the glass transition of polymers was studied in detail by Kovacz. Figure 8.1 shows the time dependence curve he obtained for the difference between the volume of polymer V_t and its equilibrium volume at the same temperature V_∞. It can be seen from the figure that with increasing temperature the polymer approaches its equilibrium state faster and faster. The curves can be superimposed by shifting them along the time axis. This signifies equivalence of the effect of time and temperature on the establishment of equilibrium, which is an important feature of relaxation (Chap. 7). The relaxation nature of glass transition is associated with the slowness of regrouping of chains and supermolecular structures near T_g.

Volkenshtein and coworkers demonstrated the cooperative nature of processes occurring during glass transition, i.e., that the property of any part of the system depends on its neighbours.

Thus, the relaxation kinetic nature of glass transition is obvious.

It follows from the given data that we always obtain a polymer in a nonequilibrium state when it is rapidly cooled. But at temperatures which are considerably lower than its T_g, a polymer may remain in this nonequilibrium state infinitely. Moreover, for noncrystallizing polymers, the glassy state is the only possible solid state.

Proceeding from this, Gibbs and Di Marzio believe that, despite the absence of a crystalline lattice, at a certain sufficiently low

temperature T_2, where the relaxation processes occur very slowly, the glassy state can be regarded as an equilibrium, thermodynamically stable state. The temperature T_2 is the lower limit of glass-transition temperatures T_g obtained experimentally at infinitely slow cooling.

According to the ideas developed by these authors, a second-order phase transition occurs at this temperature T_2 in the amorphous state.

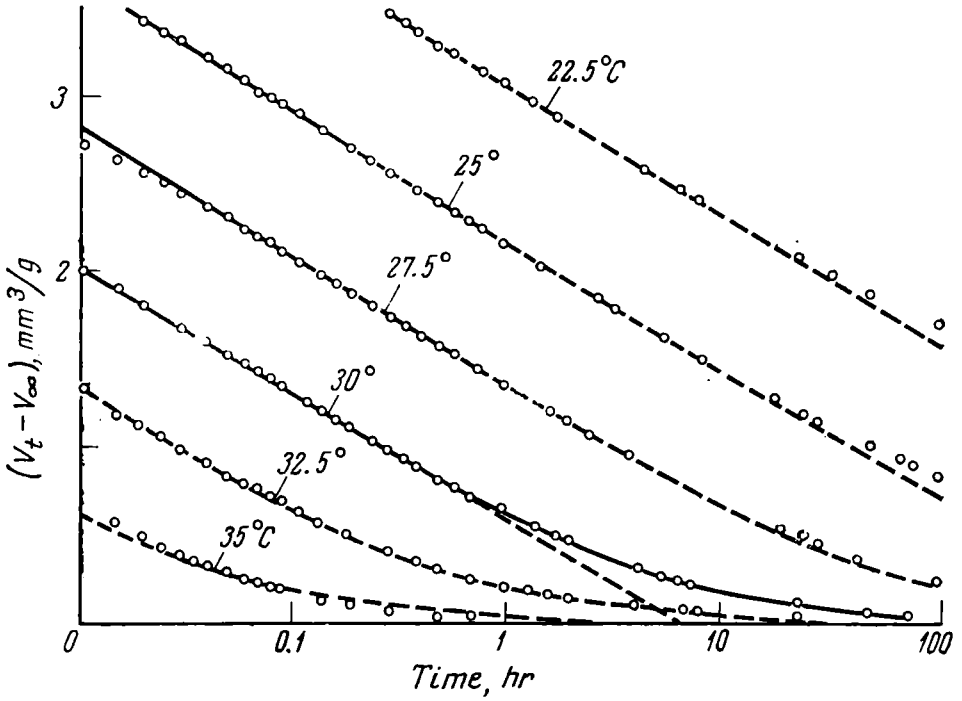

Fig. 8.1. Time dependence of difference between volume of poly(vinyl acetate) at temperature t and its equilibrium volume at that temperature $(V_t - V_\infty)$

This viewpoint must be specified. A glassy state is not an equilibrium state, but a *metastable* state, i.e., a state in which a system remains infinitely long and a new phase does not appear in it (p. 173). From the standpoint of thermodynamics, we have the right to regard both equilibrium phases and metastable phases as stable ones, since they possess common properties which distinguish them from unstable phases. However, phase transitions at temperatures far lower than the glass-transition temperature are scarcely probable.

8.2. MECHANISM OF GLASS TRANSITION

The first attempt to explain the mechanism of glass transition is due to Zhurkov. According to his ideas the possibility of glass transition of high polymers, like that of low-molecular substances,

depends upon the ratio between the energy of interaction (intra- and intermolecular) and the energy of thermal motion of their units. The energy of intermolecular interaction is either independent of temperature, or depends on it insignificantly. But the energy of thermal motion (kT) decreases sharply with decreasing temperature and at certain definite values of the latter becomes insufficient to overcome the intra- and intermolecular interactions. This increases the viscosity of polymer and decreases the intensity of thermal motion of its units, i.e., increases chain rigidity.

The effect of intermolecular interaction on the ability of polymers to become glassy can be observed on polar polymers, because the energy of interaction between polar groups is several times higher than between nonpolar ones. For example, the interaction energy between chlorine atoms of neighbouring chains is 6 kcal/mole, whereas that between CH_2 groups is only 1 kcal/mole. For this reason the links between the chlorine atoms or between other polar groups (CN, OH, etc.) of neighbouring chains are stronger and do not break unless the thermal motion is very intense. Thus, strong intermolecular interaction between separate groups results in the formation of local *crosslink points* or *nodes* in the polymer. However, in contrast to the network formed by chemical bonds (Chap. 3), this network is not constant in time, because local intermolecular bonds easily break down and form anew. The average lifetime of groups in the linked state increases with decreasing temperature and becomes commensurable with the duration of the experiment near the glass-transition temperature.

The formation of nodes somewhat decreases the mobility of contiguous chain units, i.e., limits their thermal motion. For this reason, even in the presence of a comparatively small number of long-lived nodes the entire system becomes more rigid. Thus, cooling results in the formation of a rather stable structure with a fixed random arrangement of polymer molecules relative to one another, and below the glass-transition temperature (T_g) the polymer acquires the properties of a solid. If a polymer is heated above T_g, the intermolecular crosslinks break down, increasing the mobility of the units and the flexibility of the chains, and the polymer passes into the rubber-like state.

Strong nodes form practically only between polar groups, and therefore the more polar groups a polymer contains, the higher should be its glass-transition temperature.

The formation of local intermolecular bonds has been proved by infrared spectroscopy. The IR absorption spectra of poly(vinyl alcohol), gelatin, and several polyamides were studied at temperatures ranging from 0 to 150 °C. Maxima were observed in the spectrum of poly(vinyl alcohol) at wavelengths of 1.60 and 1.49 μ, whose position did not change when heated to 50-60 °C. On further

heating the intensity of the 1.60 μ band gradually decreases while that of the 1.49 μ band increases. At 130-150 °C a fairly sharp maximum appears on the absorption curve at 1.42 μ. The maximum at 1.60 μ is characteristic of hydroxyl groups forming hydrogen bonds, and that at 1.42 μ, of free hydroxyl groups.

It follows therefore that heating to $T > T_g$ breaks intermolecular hydrogen bonds, and cooling to $T < T_g$ makes them form.

The absorption spectra obtained enable a quantitative estimate of the concentration of "free" and "bound" groups at different stages of heating.

The results of the experiments show that in the glassy polymers studied most of the hydroxyl groups take part in the formation of hydrogen bonds. This means that in the glassy state the polymer is an unordered network.

Evidently molecular networks may form not only through hydrogen bonds, but also as a result of orientational interaction of dipoles, e.g., interaction between chlorine atoms or nitrile or other polar groups.

A second mechanism of glass transition, differing from that just described and investigated by Kargin and Slonimsky, is associated with increase in chain *rigidity* upon cooling. In reality the two mechanisms are evidently superimposed on each other, i.e., cooling increases both intermolecular interaction (forming strong "nodes" between the chains) and the rigidity of the chains themselves.

Glass transition is connected with the polymer attaining a definite free volume. For most polymeric systems the free volume fraction at the glass transition temperature $f_g = V_f^g / V_{sp}^g = 0.025 \pm 0.003$ (where V_f^g and V_{sp}^g are the free and specific volumes of the substance at the glass-transition temperature). The fraction of the free volume f_g can be calculated for any temperature above T_g from the equation

$$f_g = 0.025 + \alpha_s (T - T_g) \tag{8.1}$$

where α_s is the coefficient of thermal expansion of the polymer above T_g, which is close to the value of α_s for low-molecular liquids.

8.3. METHODS OF DETERMINING THE GLASS-TRANSITION TEMPERATURE OF POLYMERS

The transition of a polymer from the rubber-like to the glassy state is accompanied by a gradual change in its physical properties (volume, density, dielectric and mechanical properties, etc) and the temperature of the transition can be determined by stu-

dying the variation of these properties with temperature. The most popular methods are based on studying the following properties:

(1) specific volume (dilatometric method),
(2) heat capacity,
(3) modulus of elasticity,
(4) deformation.

8.3.1. Measuring Specific Volume (Dilatometric Method)

Figure 8.2 is a typical specific volume vs. temperature curve for an amorphous polymer. The region *OB* represents the rubber-like state of the polymer, where the coefficient of volume expansion is approximately the same as for the low-molecular liquid. The region *AO* is the glassy state, where the coefficient of volume expansion is smaller than in the rubber-like state (p. 177). That is why *AO* slopes more gently with respect to the temperature axis than *OB*. The transition from the volume expansion coefficients characteristic of the rubber-like state to those characteristic of the solid does not occur jumpwise, but gradually over a certain range of temperatures. The average temperature of this range is accepted as the glass-transition temperature of the polymer.

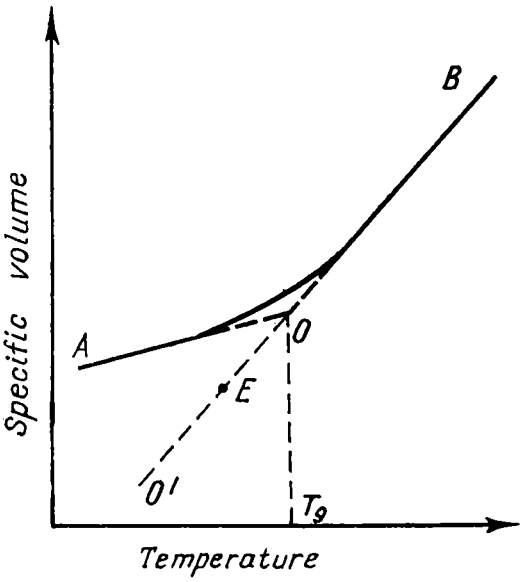

Fig. 8.2. Temperature dependence of specific volume of a polymer

The line *OB* (Fig. 8.2) corresponds to an equilibrium state.

When the temperature is lowered, the intensity of thermal motion of the units decreases and the relaxation time increases exponentially with temperature [see Eq. (7.37), p. 190], and there is no time enough for equilibrium structure to be attained. Hence, *AO* corresponds to nonequilibrium volumes.

If it were possible to cool the material so that equilibrium were reached at each temperature, the v vs. T dependence would be represented by *O'B*. It is evident from the figure that the measured specific volumes (*AO*) are always higher than the equilibrium values and the lower the temperature, the greater the difference.

To reach an equilibrium state the material must be held for a long time at the assigned temperature, i.e., annealed *. The lower the temperature, the longer the annealing time.

In a study of the effect of annealing on volume relaxation of low-molecular glasses it was found that when a selenium specimen was cooled rapidly from 35 to 30 °C it did not have time to change its structure, and the measured volume was larger than the equilibrium value. When the specimen was annealed for 3-4 hrs at 30 °C, its specific volume decreased gradually to the equilibrium value. The time needed to reach equilibrium volume decreases with rising temperature.

If selenium is annealed successively at stepwise varying temperature, i.e., cooled very slowly, its specific volume vs. temperature dependence will be a straight line without a break (Fig. 8.3). A similar phenomenon is observed when silicate glasses are annealed.

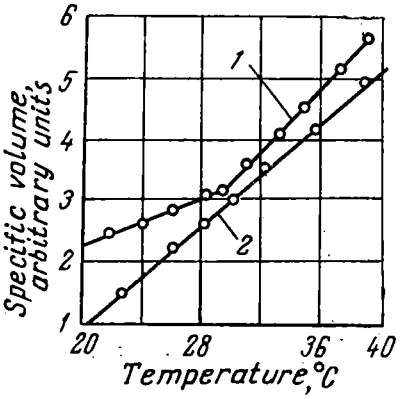

Fig. 8.3. Temperature dependence of specific volume of selenium:
1—fast cooling; *2*—slow cooling

If a polymer is cooled sufficiently slowly, it can be obtained in the equilibrium state at a temperature below its glass-transition temperature (point E in Fig. 8.2). The lower the temperature, the more time this requires. Thus, according to the data of Alfrey *et al.* establishment of the equilibrium structure of high-molecular polystyrene at 60 °C requires 3 hr (17 hr, according to others, which is more likely). At lower temperatures it takes much more time, as can be shown by a simple calculation.

Substituting into Eq. (7.37) the value of $\Delta U = 60\,000$ cal/mole (the activation energy of rubber-like deformation) and taking the relaxation time at 60 °C to be 17 hr, the relaxation time at 20 °C is about 100 years. Therefore at temperatures much below the glass-transition temperature no annealing, however long, can practically bring the polymer to its equilibrium state. But the longer annealing is done, the closer will the polymer approach this state.

Thus, from the above reasoning it follows that *the slower a polymer is cooled, the lower will be its glass-transition temperature.* However, it takes a very long cooling time to cause a noticeable change in T_g. For instance, a change in rate of cooling of one order of magnitude will alter the glass-transition temperature by

* *Annealing* means holding the material for a long time at a definite temperature (in contrast to *hardening* which involves very rapid cooling).

only a few degrees. That is why the numerical values of T_g determined dilatometrically by different workers at the usual cooling rates are, as a rule, very close.

8.3.2. Measuring Heat Capacity

The heat capacity of a body depends on the number of its internal degrees of freedom, i.e., on the possible modes of motion of its molecules. A substance in the liquid state has more degrees of

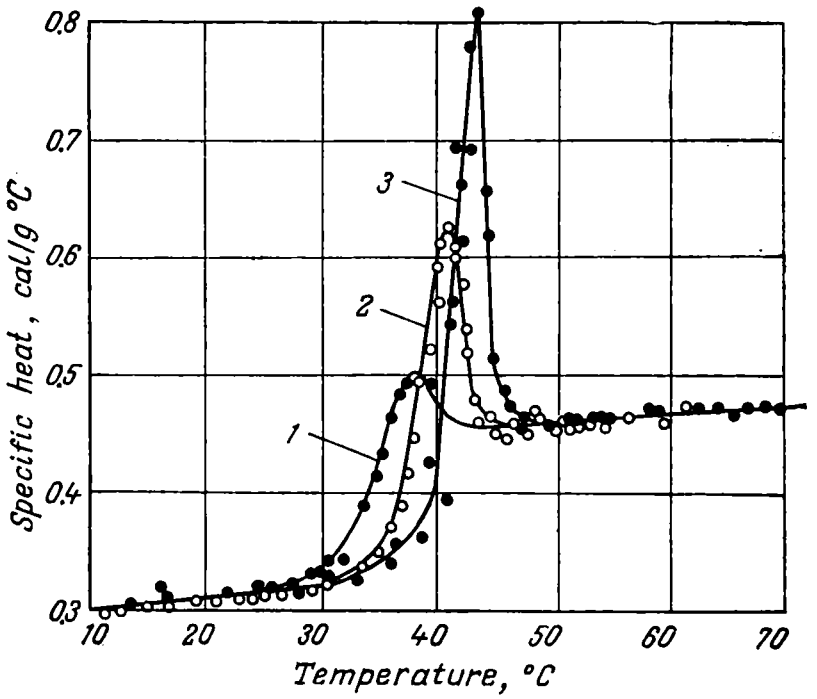

Fig. 8.4. Temperature dependence of specific heat of poly(vinyl acetate) at various rates of heating:
1—rate of heating 0.1 deg/min; *2*—0.4 deg/min; *3*—1.5 deg/min

freedom than in the solid (solids have no translational or rotational motion). Therefore when a liquid is heated, the heat absorbed is expended on a larger number of degrees of freedom, and hence the heat capacity of a substance in the liquid state is always greater than in the solid.

Cooling decreases the heat capacity of a substance. If cooling is accompanied by crystallization, the heat capacity changes jumpwise at the crystallization temperature.

Glass transition is characterized by a gradual change in heat capacity with temperature.

Sometimes the glass transition of amorphous polymers involves a change of heat capacity with temperature, described by curves with maxima (Fig. 8.4).

Such a temperature dependence of heat capacity is typical of second-order phase transitions (see p. 149), but in these cases the position of the maximum on the curve (with respect to the temperature axis) is independent of the rate of heating. But in the glass transition of polymers [e.g., poly(vinyl acetate), poly(methyl methacrylate), etc.] the height and position of the maxima on the c_p vs. T curves depend very greatly on the rate of heating. It is evident from Fig. 8.4 that the greater the rate of heating of the sample, the higher will be the peak. With slow heating the maxima vanish entirely. This means that the observed temperature dependence of heat capacity of polymer is a result of relaxation processes occurring in the polymer. Let us examine this phenomenon in more detail.

When a body is heated, the heat absorbed is expended on regrouping its molecules. If the time required for such regroupings (relaxation time τ) is smaller than the time during which the heat is delivered to the body, the molecules of the sample will have time to regroup and its heat capacity will change gradually with temperature (see Fig. 8.4). If heat is delivered quickly, the molecules will not have time to regroup and the heat capacity will not change. With increasing temperature the relaxation time decreases, and at a certain temperature τ becomes smaller than the time during which the heat is supplied; the regrouping will take a very short time, which corresponds to a sharp increase in heat capacity.

On further heating the heat delivered is expended on molecular regroupings corresponding to the given temperature, and the heat capacity will decrease to its equilibrium value, giving a maximum on the curve. The faster the polymer is heated, the higher will be the temperature at which its units regroup instantaneously, and the higher will be the maximum on the curve. With decreasing rate of heat delivery the height of the maxima decreases. If heating is done sufficiently slowly, no maxima will be observed at all on the c_p vs. T curves.

The maxima on the c_p vs. T curves correspond to small relaxation times, i.e., to transition of the polymer from the glassy to the rubber-like state. The average temperature of the region wherein the heat capacity changes sharply may be accepted as the glass-transition temperature of the polymer.

The effect of relaxation processes should be taken into account when the heat capacity of polymers is being measured. When measurements are being made, the heating rate should not exceed 0.1-0.2 deg/min. Then, a change in heat capacity with temperature has a characteristic form which is represented in Fig. 8.5. In the low-temperature range, the temperature dependence of heat capacity is monotonous and close to rectilinear. This is characteristic

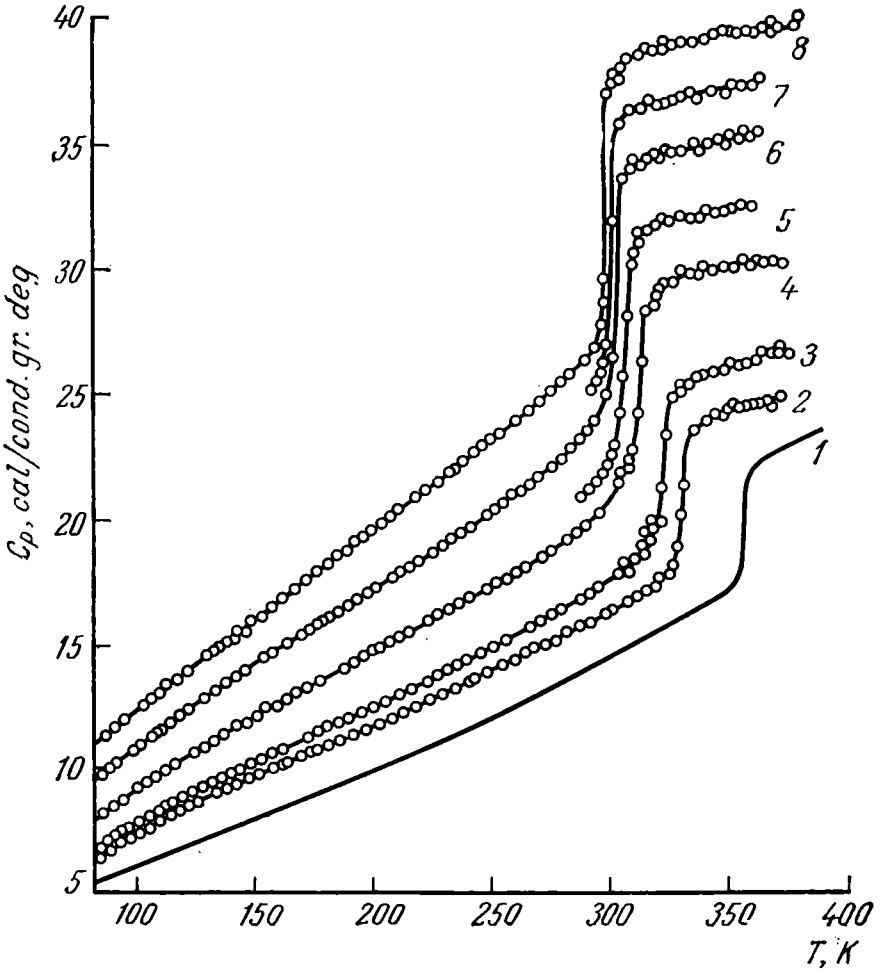

Fig. 8.5. Temperature dependence of heat capacity of vinyl chloride-vinyl acetate copolymers:
1—0; *2*—12.3; *3*—23.8; *4*—47.3; *5*—56.3; *6*—74.8; *7*—87; *8*—100 mol. VA

of all amorphous polymers. The curve then rises due to the transition from a glassy state to a rubber-like state, and heat capacity linearly depends on temperature in the high elasticity region.

8.3.3. Measuring the Modulus of Elasticity

The modulus of elasticity of a polymer in the rubber-like state is very low (p. 181). The glassy state is characterized by high values of the modulus of elasticity.

The transition of polymers from the rubber-like to the glassy state is accompanied by a change in the modulus of several orders of magnitude (Fig. 8.6). The average temperature of this region is the glass-transition temperature.

The modulus vs. temperature curves of all amorphous polymers are of approximately the same shape, and they can be superim-

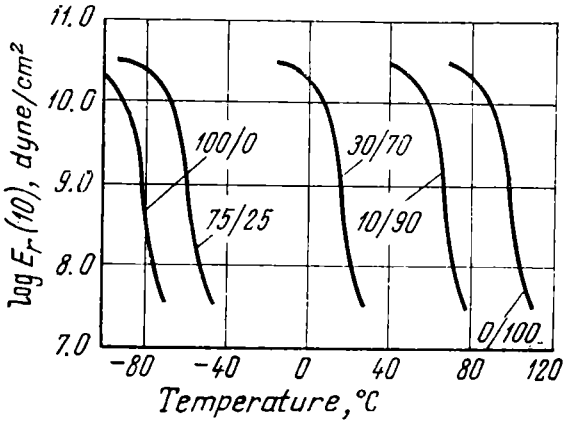

Fig. 8.6. Temperature dependence of relaxation modulus for butadiene-styrene copolymers. Numbers at curves are butadiene-styrene ratios

posed by shifting them horizontally along the temperature axis until their T_g coincide.

8.3.4. Measuring Deformations. Thermomechanical Method

The method consisting in measuring the temperature dependence of the deformation of a polymer is called the *thermomechanical method.*

A deformation vs. temperature curve at constant load is called a *thermomechanical curve.* Such curves for polymers have already been examined (Fig. 7.8).

Large deformations at low stresses are characteristic of the rubber-like state. The equilibrium rubber-like deformation is independent of temperature (p. 194); but at low temperatures rubber-like deformation does not have time to develop owing to its relaxation nature. For this reason the strain $\varepsilon_{el,\,t}$ decreases with declining temperature and at a certain temperature small stresses may cause only small elastic deformations (see Fig. 7.9). The temperature at which the deformation becomes equal to the elastic deformation, i.e., the temperature at which the material completely loses its rubber-like properties, corresponds to the glass-transition temperature of polymer.

It should be noted that this temperature depends greatly on the frequency of deformation. The higher the frequency of loading, or deformation rate, the higher will be the glass-transition temperature. This leads to a very important practical conclusion, namely: one and the same material may display rubber-like properties at low deformation frequencies (at long loading times) and behave

like a glassy substance at high frequencies. This fact should be taken into account when using articles made of polymeric materials (e.g., rubber articles), if they are subject to dynamic or impact loads at low temperatures. For the same reason tests carried out under static conditions may not correspond to the conditions under which the articles are used.

In plant practice, frost resistance of rubbers is very often characterized by what is known as the *coefficient of frost resistance*, equal to the ratio of strain values at a certain low temperature and at room temperature, e.g.,

$$K = \frac{\varepsilon_{-40\,^\circ C}}{\varepsilon_{+20\,^\circ C}}$$

The measurements are carried out while extending slowly.

The resulting frost resistance coefficients cannot characterize the behaviour of rubbers operating under impact loads or periodic deformations. In such cases it is recommended to determine T_g of the polymer at various frequencies of loading.

In practice it is not always important to know the temperature at which the material loses its rubber-like properties completely, i.e., the glass-transition temperature, because in a number of cases a decrease of rubber-like properties by one half already renders the article useless. Therefore, it is sufficient to determine the temperature at which the deformation value drops two-fold compared to its initial value; this temperature is known as the *half-strain temperature.*

According to Eq. (7.45), a ten-fold increase of frequency will raise the half-strain temperature about 5 or 7 °C upon slow deformation and 7 or 9 °C upon fast deformation. Therefore, on passing to very high frequencies of loading, the half-strain temperature (as well as T_g) may be tens of degrees higher than the values determined under static conditions.

In a wider temperature range, the thermomechanical curve of an amorphous linear polymer of high molecular mass has three portions (Fig. 8.7), corresponding to three physical states. The first portion (*I*) corresponds to the glassy state, where not very high stresses * cause small strains, the second (*II*) represents the rubber-like state with its large recoverable deformations. On these deformations is superimposed the flow deformation, which increases with rising temperature. At fairly high temperatures relative displacements of entire chains become easy enough to enable what is known as *true flow* of the polymer to occur. The polymer passes from the rubber-like to the viscofluid state. This transition is accompanied by a sharp increase in deformation (portion *III*).

* It will be shown in Chap. 9 that under large stresses glassy polymers are capable of deforming very greatly.

The temperature of the transition from the rubber-like to the viscofluid state (*flow temperature* T_f) is not a definite point, but the average temperature of the range within which true flow of the polymer develops.

It should be noted that not every sharp increase in deformation can be identified with true flow. With some polymers increasing the slope of the ε vs. T curve is a result of recoverable rubber-like deformation, which develops rapidly with rising temperature. To make sure that the increase in slope of the curve is evidence of the

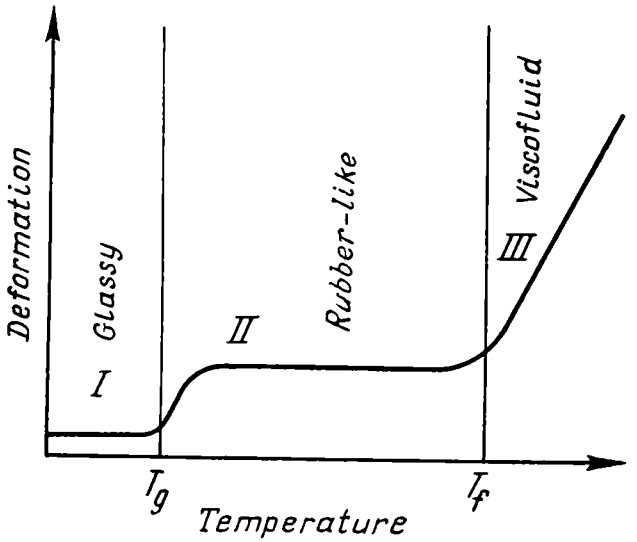

Fig. 8.7. Thermomechanical curve of a polymer

development of flow, experimental data must be available, confirming that the large strains are irrecoverable. Only in this case can the flow temperature be determined from the thermomechanical curve.

The flow temperature of a polymer, like its glass temperature, depends on the conditions of deformation. For this reason the flow temperatures of polymers of different structure can be compared only if they have been determined under the same conditions (equal stresses, equal heating rates, etc.).

The transition of a polymer from the rubber-like to the viscofluid state cannot be detected on its temperature vs. volume or temperature vs. heat capacity curves. But the transition is fairly distinct on deformation vs. temperature graphs.

8.4. STRUCTURAL AND MECHANICAL GLASS TRANSITION

It follows from the above that the glass transition temperature can be determined from the changes in different physical properties of a polymer depending on temperature. When measuring these

changes, however, allowance must be made for the time factor (rate of heating or cooling, loading time, etc.) owing to the relaxation nature of the glass-transition process. Upon fairly slow cooling or with a fairly long loading time the glass-transition temperatures obtained for the same polymer by different methods usually coincide. For instance, the break on the specific volume vs. temperature curves will appear in the same temperature region as a sharp increase in the modulus. This is evidence that the molecular regroupings occuring upon cooling and upon rubber-like deformation are of a similar nature. But there is also a certain difference, and this made it necessary to introduce the concepts of structural and mechanical glass transition.

Structural or *true glass transition* is the process of formation of nonequilibrium structures when the polymer is cooled below a definite temperature (T_g).

Mechanical glass transition is associated with the behaviour of the material in a mechanical field of various frequencies at the same temperature. Thus, increasing the frequency of loading from 0.1 to 1000 vibrations per minute causes a shift of the glass-transition temperature of 30 to 40 °C.

It is possible to imagine a frequency of loading (e.g., ultrasonic frequency) at which molecular regroupings will not have time to occur in cured or uncured rubber even at room temperature. Under such conditions the material, which is elastic when the loading is slow, will display properties corresponding to the solid glassy state. This phenomenon, which occurs at temperatures tens of degrees above the glass-transition temperature, has become known as mechanical glass transition. During mechanical glass transition the material retains its equilibrium structure.

8.5. EFFECT OF MOLECULAR MASS OF POLYMER ON ITS GLASS-TRANSITION TEMPERATURE AND ON FLOW TEMPERATURE

With increasing molecular mass of a polymer the glass-transition temperature increases very quickly at first, then more slowly, and finally reaches a constant value. Figure 8.8 is a typical curve showing the dependence of T_g on the molecular mass of polymer. Two relations have been proposed to describe this dependence:

$$T_g = T_{g,\infty} - \frac{k}{M} \qquad (8.2)$$

$$\frac{1}{T_g} = \frac{1}{T_{g,\infty}} + \frac{k'}{M} \qquad (8.3)$$

where T_g = absolute glass-transition temperature of polymer of given molecular mass M

$T_{g,\infty}$ = limiting value of glass temperature at infinite chain length

k and k' = constants.

The molecular mass at which the glass temperature of a polymer becomes constant depends on its kinetic chain flexibility. In

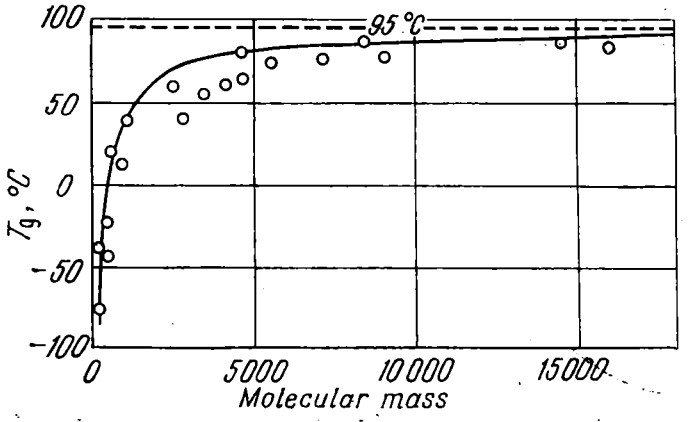

Fig. 8.8. Glass-transition temperature versus molecular mass of polystyrene

polymers with very flexible chains (polyisobutylene) T_g becomes constant, beginning from $M = 1000$; in polymers with chains of low kinetic flexibility the glass transition temperature becomes constant at $M = 12\,000$-$40\,000$ and more.

The effect of molecular mass on the flow temperature of polymers was first studied by Kargin and Sogolova. The thermomechanical curves for polymers of the same homologous series are shown schematically in Fig. 8.9. It is evident from the figure that low-molecular polymer homologues can exist only in two states, namely, the glassy and the liquid, their glass transition and flow temperatures coinciding. The transition from the glassy to the liquid state is accompanied by a sharp increase in deformation. With increasing molecular mass the curve shifts towards higher temperatures, i.e., the glass-transition temperature of the polymer rises. At a certain molecular mass the transition temperature "splits" into T_g and T_f, and three portions appear on the curve. With further increase of molecular mass the glass-transition temperature remains constant, whereas the flow temperature continues

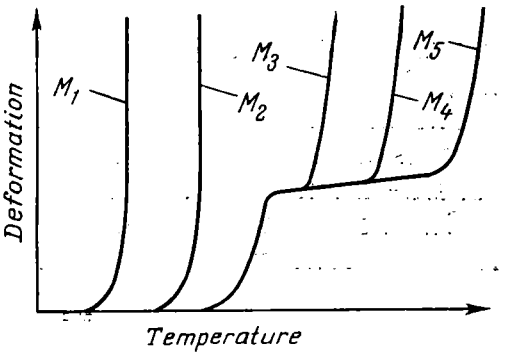

Fig. 8.9. Thermomechanical curves of polymers of the same homologous series ($M_5 > M_4 > M_3 > M_2 > M_1$). $e_{el} = 0$

to increase, hence, the higher the molecular mass of a polymer, the greater is the difference $T_f - T_g$ characterizing the temperature range of rubber-like elasticity. The regularity illustrated by Fig. 8.9 is common to all amorphous linear polymers. The molecular mass, at which the transition temperature "splits" into T_g and T_f, depends on the chain flexibility: the more rigid the chain, the higher will be the molecular mass at which the transition temperature "splits". Thus, in polyisobutylenes rubber-like strain appears at as low a molecular mass as $M \approx 1000$, whereas in polystyrene it appears only at $M \approx 40\,000$.

Thus, high-molecular polymers with flexible chains possess low glass temperatures and high flow temperatures, i.e., a wide temperature range of rubber-like elasticity (from —70 to +200 °C). High-molecular polymers with more rigid chains have high glass-transition temperatures and a narrow rubber-like elasticity range (from 100 to 160 °C).

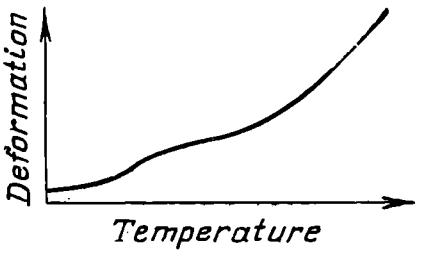

Fig. 8.10. Thermomechanical curve for polydisperse polymers

Polymers with still less flexible chains have very high T_g and their $T_f - T_g$ is so small that they practically do not display rubber-like properties even at increased temperatures. In this case one often speaks of *softening* of the polymer, i.e., of direct transition from the glassy to the viscofluid state.

The flow temperature of amorphous linear polymers always increases with increasing molecular mass. This should be taken into consideration when fabricating them.

On the basis of experimental data Kargin and Slonimsky derived the following theoretical equation *

$$\log M = \log M_s + \frac{B(T_f - T_g)}{C + (T_f - T_g)} \qquad (8.4)$$

where M = molecular mass of a polymer
M_s = molecular mass of chain segment
T_f = flow temperature
T_g = glass-transition temperature
B and C = empirical constants depending on the deformation regime and chemical nature of the polymer.

In the case of polyisobutylenes, for example, Eq. (8.4) becomes:

$$\log n = 1.35 + \frac{6.68(T_f - T_g)}{263 + (T_f - T_g)} \qquad (8.5)$$

where n is the degree of polymerization of the polyisobutylene.

* Equation (8.4) is an analogue of the WLF equation, but was obtained at a much earlier date.

Equation (8.5) can be used for calculating the molecular mass of polyisobutylene, if the thermomechanical curve was plotted with the aid of the same instrument (dynamometric balance) and under the same conditions for which the numerical values of the constants B and C were found.

Thus, using the thermomechanical method it is possible, in principle, to determine the molecular mass of a polymer without dissolving it.

The thermomechanical curves of polydisperse polymers differ slightly from those of polymers of comparatively uniform molecular mass distribution, that of a polydisperse polymers being "smoother" (Fig. 8.10). This is due to the fact that polymer fractions of different molecular masses pass into the viscofluid state at different temperatures.

8.6. CHEMICAL CONSTITUTION OF POLYMERS AND GLASS-TRANSITION TEMPERATURE

The glass-transition temperature depends on the structure and polarity of a polymer, which affects both chain flexibility and intermolecular interaction energy.

Nonpolar polymers possess high chain flexibility (Chap. 4), and since their potential energy barriers for rotation are not high, their chains remain flexible down to very low temperatures. For this reason nonpolar flexible-chain polymers have low glass-transition temperatures of the order of —70 °C (Table 8.1).

TABLE 8.1. *Glass Transition Temperatures of Some Polymers and Methods of Their Determination*

Polymer	T_g, °C	Method
Natural rubber	—70	By change in heat capacity
	—70	By change in deformation
Polyisobutylene	—74	By change in heat capacity
	—75	By change in deformation
Butyl rubber	—69	Ditto
Polyisoprene (СКИ)	—70	Ditto
Polybutadiene (СКБ)	—40	Ditto
Polychloroprene	—40	Ditto
Polystyrene	81	Dilatometry
	100	By change in deformation
Poly(vinyl chloride)	80	Ditto
Poly(methyl methacrylate)	100	Ditto
	125	Ditto

Table 8.1 (*cont'd*)

Polymer	T_g, °C	Method
Poly(vinyl acetate)	28	By change in heat capacity
Poly(vinyl alcohol)	85	Ditto
	130	By change in deformation
Polytetrafluoroethylene	—150	Ditto
Silicone rubber	—120	Ditto
Cellulose	Above decomp. temp.	Ditto
Cellulose nitrate	Ditto	Ditto
Cellulose acetate	Ditto	Ditto
Polyacrylonitrile	Ditto	Ditto
Poly(vinylidene chloride)	—17	Ditto

The polarity of the macromolecules also affects the flow temperature of a polymer substantially. Since polar chains interact more strongly than nonpolar ones, polar polymers are more viscous. Therefore, to cause displacement of whole chains a polar polymer has to be heated to a higher temperature; this means that its flow temperature is higher.

8.6.1. Estimation of Kinetic Chain Flexibility from Thermomechanical Curves

The *kinetic chain segment* can be estimated from the thermomechanical properties of polymers and their glass and flow temperatures. Thus, it is evident from Fig. 8.8 that at a certain molecular mass of a polymer the glass temperature stops changing with increasing molecular mass and the polymer begins to exhibit the first signs of the rubber-like state, or in other words, chain flexibility. Chain flexibility is displayed in polymers of different chemical constitution at different degrees of polymerization. In nonpolar polymers (e.g., polyisobutylene) chain flexibility appears at a molecular mass of as low as 1000 ($n = 20$), i.e., at this chain length the glass-transition temperature does not coincide with the flow temperature. In polar polymers [e.g., poly(vinyl chloride)] the transition temperature "splits" into T_g and T_f and the glass temperature becomes independent of molecular mass at much higher molecular masses ($M = 12\,000$).

Obviously, the length at which a chain begins to exhibit flexibility can serve as an estimate of kinetic chain flexibility. This chain

length coincides with the size of chain segment, meaning the kinetic or mechanical segment, in contrast to the thermodynamic segment discussed in Chap. 4 in connection with the methods of its estimation. The *mechanical* (*kinetic*) *segment* is the minimum length of molecular chain of a polymer, at which it just displays kinetic flexibility. The mechanical segment is a measure of the kinetic flexibility of a chain: if the segment is small, the chain is flexible; if it is large, the chain is stiff. Polymers with a large number of strongly polar groups (cellulose, etc.) have low kinetic chain flexibility and their segment size is greater than that of their macromolecule.

The mechanical segment is no definite physical repeating section in a long macromolecule. The real sections are monomeric units vibrating at one amplitude or another. The segment is only an equivalent quantity characterizing the kinetic flexibility of a polymer chain.

The presence of sparsely spaced polar groups (C—Cl) increases intermolecular interaction and raises the glass-transition temperature. For example, the glass temperature of polychloroprene is about —40 °C. Increasing the amount of polar groups raises its glass-transition temperature, as can be observed on the example of acrylonitrile-butadiene copolymers:

	T_g, °C
CKH-18	—50
CKH-26	—30
CKH-40	—20

A very important factor is the arrangement of the polar groups: if the electric fields of the polar groups compensate one another, the chains will possess sufficient flexibility and the glass-transition temperature will therefore be low (Chap. 4). This can be illustrated by the following examples. Compare poly(vinyl chloride) and poly(vinylidene chloride). The polar C—Cl bonds of the former are arranged unsymmetrically, its chains are rigid, and its glass temperature is +80 °C. In the latter, the polar C—Cl bonds are symmetrically arranged, its chain is flexible (Chap. 4) and its glass temperature is —17 °C. The glass-transition temperature of polytetrafluoroethylene, a polymer whose polar C—F bonds are all symmetrically arranged, is —150 °C. The glass temperatures of strongly polar polymers with unsymmetrically arranged polar groups (cellulose, cellulose acetate and nitrate, polyacrylonitrile, etc.) are in the very high temperature region, often even above their decomposition temperature.

The glass-transition temperature is affected by the presence of large-size substituents, which hinder rotation of the units, so that the chains have practically no flexibility. Obviously, for chain

flexibility to appear in this case the polymer has to be heated to higher temperatures, i.e., the glass temperature of such polymers should be rather high (T_g of polystyrene is 100 °C). The glass-transition temperature of butadiene-styrene copolymers increases gradually with increasing number of phenyl residues in the chain:

	T_g, °C		T_g, °C
СКС-10	−80	СКС-70	−4
СКС-30	−72	СКС-80	+14
СКС-50	−46	СКС-90	+34
СКС-60	−24		

The presence of a phenyl and a methyl substituent at the same carbon atom causes still greater steric hindrances and increases the glass temperature still more. Thus, poly-α-methylstyrene has a higher glass-transition temperature than polystyrene. The same is true of polymers with a methyl and a COOR group at the same carbon atom. The glass-transition temperatures of polymethacrylates are much higher than those of polyacrylates:

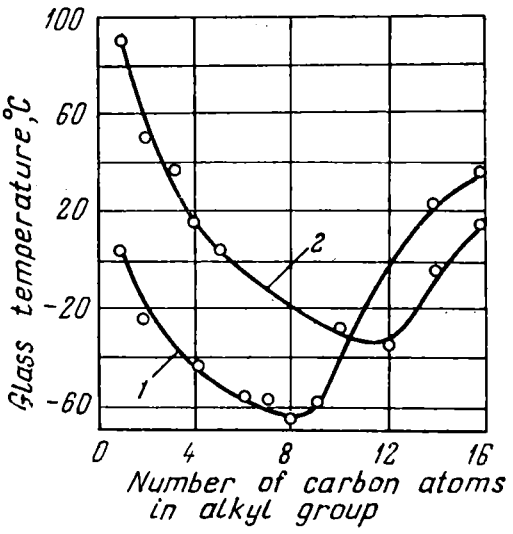

Fig. 8.11. Dependence of glass-transition temperature of *n*-alkyl acrylate (*1*) and *n*-alkyl methacrylate (*2*) polymers on size of alkyl group

	T_g, °C
Poly(methyl acrylate)	7
Poly(ethyl acrylate)	−20
Poly(butyl acrylate)	−40
Poly(methyl methacrylate)	100
Poly(ethyl methacrylate)	50
Poly(butyl methacrylate)	8

If the polar groups are screened by nonpolar ones, the energy of intermolecular interaction is lower and so is the glass-transition temperature. This accounts for the low glass temperature of silicon rubbers, whose intermolecular interaction is low (interaction occurring between alkyl groups). In polyacrylates and polymethacrylates the polar —C—O—C— bond becomes screened with increasing size of the alkyl radical and their T_g declines. However, above a certain size of alkyl radical, T_g increases again due to steric hindrances caused by the presence of large substituents (Fig. 8.11).

Strong chain branching also causes steric hindrances, which is the reason why branched polybutadienes, for instance, have higher glass temperatures than linear ones.

The glass-transition temperatures of copolymers can be calculated by the formula:

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g,1}} + \frac{\omega_2}{T_{g,2}} \tag{8.6}$$

where $T_{g,1}$ and $T_{g,2}$ = glass temperatures of the corresponding homopolymers

ω_1 and ω_2 = mass fractions of a monomer residues in copolymer.

The glass temperatures of crystalline polymers are always below their crystallization temperatures. Mostly T_g (°K) of a crystalline polymer is 0.5-0.67 of its temperature of crystallization. However, the glass-transition temperatures of some crystalline polymers, e.g., polytetrafluoroethylene, are much lower than one would expect from this relation (see Table 8.1).

8.7. PRACTICAL IMPORTANCE OF THE THERMOMECHANICAL METHOD

The thermomechanical method has become very popular in recent years. Its advantages are simplicity and the possibility of

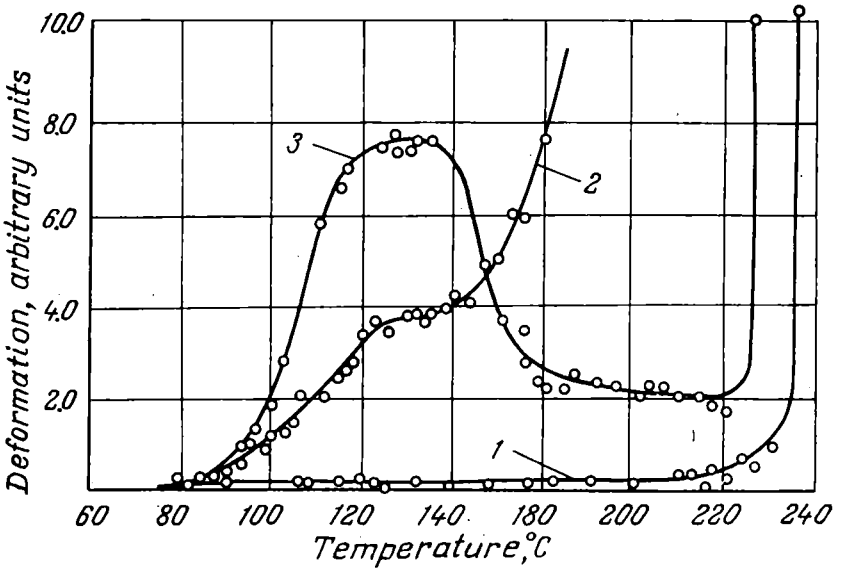

Fig. 8.12. Thermomechanical curves of isotactic and atactic polystyrene:
1—isotactic crystalline polystyrene; *2*—atactic polystyrene; *3*—isotactic amorphous polystyrene

determining quickly such important characteristics of polymeric materials as glass-transition and flow temperatures of amorphous linear polymers. It may be used to study the deformation properties of crystalline polymers (Fig. 8.12).

Below T_{cryst} a crystalline polymer behaves like a solid under low stresses (its strain being very small); above T_{cryst} the deformation increases sharply. As can be seen from Fig. 8.12, the thermomechanical curves for crystalline and amorphous polymers differ considerably from one another.

Depending on molecular mass, a crystalline polymer may pass over to a viscofluid state (when the value of M is small) or to a rubber-like state (when the value of M is high) as temperature rises.

Of great interest is the thermomechanical curve of amorphous isotactic polystyrene (curve *3*). Such a polystyrene can be obtained in the amorphous state by cooling its melt rapidly. It follows from Fig. 8.12 that, like atactic polystyrene, amorphous isotactic polystyrene passes from the glassy to the rubber-like state at about 80-100 °C; at 130-140 °C the strain begins to decrease and continues to do so up to 220 °C, i.e., up to the temperature of crystallization, above which the strain again increases. The decrease in strain is evidence of the polymer hardening in this temperature interval, and according to X-ray data in this case hardening is accompanied by the formation of a crystalline lattice.

Thus, amorphous isotactic polystyrene is in the glassy state at temperatures below T_g. The mobility of its units is very low and no crystallization occurs. At temperatures above T_g the units become more mobile and owing to its regular structure isotactic polystyrene crystallizes (Chap. 6). After crystallizing at temperatures above T_g, it preserves its crystalline structure right up to its melting point.

The thermomechanical method can be used to establish the crosslinking ability of a polymer, to determine the temperature at which crosslinks begin to form and at which the polymer hardens completely. The rate of crosslink formation can be judged from the strains registered in a polymer at different time intervals at a constant temperature. Knowledge of all these characteristics is very important for assessing the technological properties of polymers.

The thermomechanical curves shown in Figs. 8.9-8.11 represent the deformation vs. temperature dependence only of linear polymers that do not undergo chemical changes when heated. The thermomechanical curves of polymers that become crosslinked (Chap. 3) have a different shape depending on the reaction temperature region where crosslinking proceeds at perceptible rates. If intensive crosslinking occurs above the flow temperature, the polymer passes into the viscofluid state, but as more and more chemical bonds form between the chains flow deformation decreases (curve *1*, Fig. 8.13*a*). When the number of crosslinks becomes fairly large, flow becomes impossible and the polymer passes

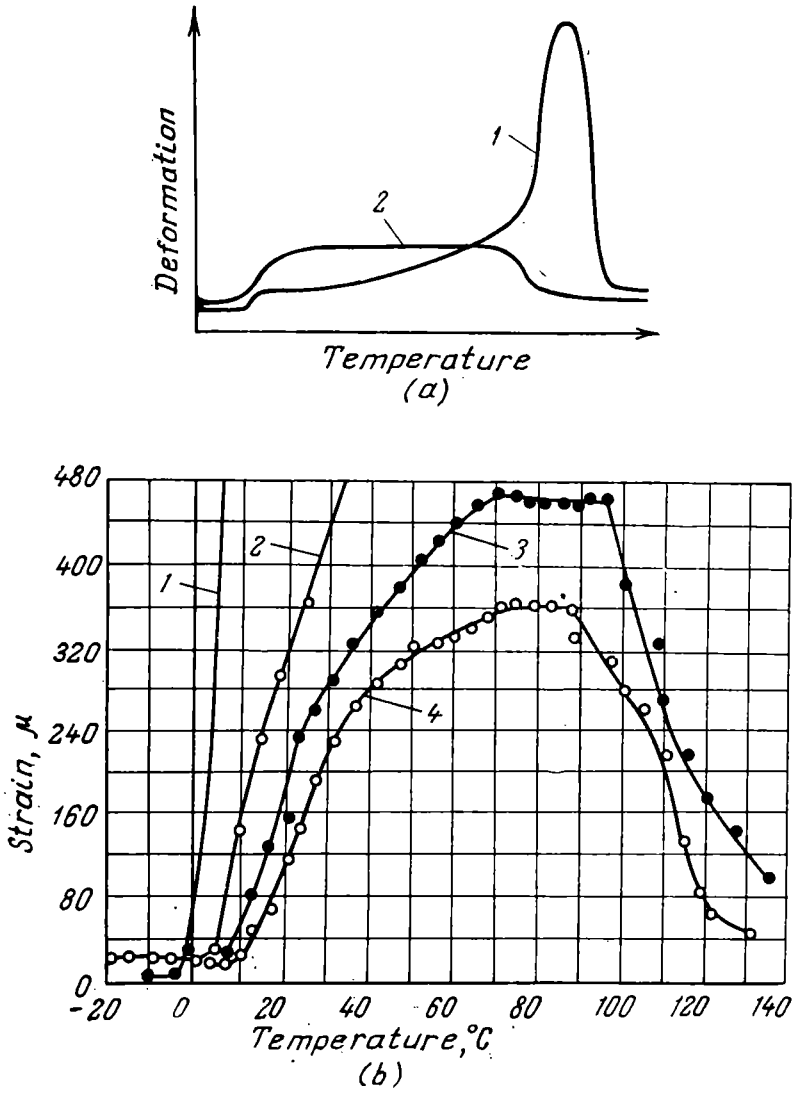

Fig. 8.13. Thermomechanical curves for structurizing polymers:
a—general shape of curves; *b*—curves of phenol-formaldehyde resins taken during polycondensation

from the viscofluid to the rubber-like, and finally to the glassy state. If crosslinks form in the polymer below the flow temperature, i.e., while the polymer is in the rubber-like state, it cannot pass into the viscofluid state at all. On further heating, owing to the increase in crosslink density, rubber-like strain decreases and the polymer passes into the glassy state (curve *2*, Fig. 8.13*a*). Thus, a crosslinked polymer can exist only in two physical states: the rubber-like and the glassy state.

As is known, crosslinking reactions may occur during polymer synthesis (Chap. 3). Polymerization and polycondensation can be

controlled by taking samples at definite time intervals and studying their thermomechanical curves (Fig. 8.13*b*).

Experiment shows that the shape of a thermomechanical curve depends on the degree of polycondensation (or polymerization). The first stage of polycondensation usually results in linear low-molecular polymers (oligomers), which pass directly from the glassy to the viscofluid state (curve *1*). The glass-transition temperature depends on the chemical nature of the polymer. Thus, for low-molecular phenol-formaldehyde resins $T_g \approx -5\,°C$, whereas

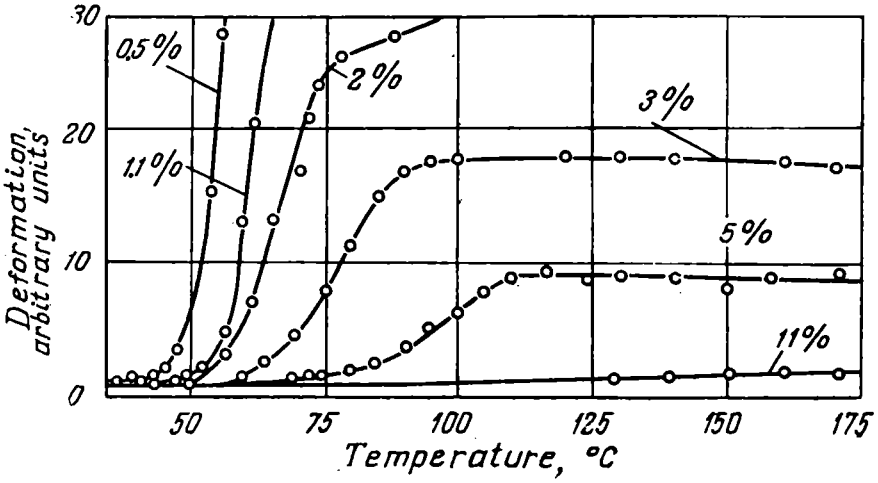

Fig. 8.14. Effect of urotropin content on hardening of phenol-formaldehyde oligomers

for tetraethoxysilane polycondensation products of the same molecular mass $T_g \approx -140\,°C$. With increasing molecular mass of oligomer the glass temperature rises (curve *2*). If the initial substances contain three or more functional groups, networks will form in the polymer, starting from a certain molecular mass ($M \approx 3000$-6000). Such a crosslinked polymer cannot exist in the viscofluid state: it becomes glassy when cooled and passes back into the rubber-like state if the temperature is raised. On further heating the rubber-like strain remains unchanged over a certain temperature range, and at a temperature of about 80 or 90 °C crosslinking begins to occur at a rapidly increasing rate and the polymer passes from the rubber-like to the glassy state, i.e., hardens (curve *3*). The longer polycondensation proceeds, the more crosslinks are formed and the smaller will be the rubber-like strain (curve *4*).

For studying polycondensation and polymerization reactions the thermomechanical method has a great advantage over the method based on viscosity measurement, because the course of the process can be judged by the viscosity only up to the beginning of crosslink formation.

By means of the thermomechanical method the effect of various substances on the hardening of polymers can be studied. Thus, Fig. 8.14 shows the effect of urotropin content on the hardening of phenol-formaldehyde oligomers. It is evident from the figure that with a urotropin content of 1.1 per cent the polymer still retains its ability to pass into the viscofluid state. With larger amounts of urotropin the polymer loses its fluidity owing to the formation of a three-dimensional network. With increasing amount of hardening agent added the glass temperature shifts towards higher temperatures; at the same time the modulus of elasticity increases. With 11 per cent urotropin the polymer displays no rubber-like strain.

The effect of plasticizers, fillers and other ingredients on the technological properties of cured and uncured rubbers and plastics can be studied in the same manner.

The thermomechanical method has been used to determine the influence of γ-radiation on silicone rubbers. It was shown that γ-rays cause the formation of networks in silicone rubbers, preventing them from crystallizing, though they usually do so at —45 °C. Irradiated crosslinked polymers do not crystallize at this temperature and retain their rubber-like properties down to —125 °C (T_g = —125 °C).

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CHAPTER 9

Deformation Properties and Mechanical Strength of Polymers

The wide usage of polymeric materials in engineering is largely due to their valuable mechanical properties and especially to their high strength coupled with large recoverable deformability. This unique combination of properties arises from the specific structure of polymers, namely, the presence in them of two kinds of linkages differing sharply in energy and length: strong chemical bonds between the atoms in the chain and much weaker intermolecular ones between the chains (p. 45).

For a long time the mechanical properties of solids were studied mainly on polycrystalline materials (metals), and as a result of these studies the main regularities of fracture of solids were established.

Fracture is rupture of the bonds between the elements of a body (atoms, molecules, or ions) resulting in *breakage* or *cleavage* of the specimen into parts. The resistance of a material to fracture is called *strength* or *mechanical strength.*

It would seem that mechanical strength should depend on the bond energy between the elements of a body. However, experiment has shown that the strength of real crystalline bodies is sometimes hundreds of times smaller than the theoretical values calculated from interatomic or interionic bond energies. This is due to the structural defects of real crystals, to the presence of a large number of defective points and cracks in any material. Fracture occurs at the most dangerous (defective) point.

In the case of polycrystalline bodies one distinguishes between brittle and tough or ductile fracture.

Brittle fracture is preceded only by recoverable (elastic) strains (p. 178). The strength of a body upon brittle fracture (*brittle strength*) is denoted by σ_{br}.

Ductile fracture is preceded by strain due to regrouping of individual structural elements of a body. In crystalline bodies and low-molecular glasses these strains are irrecoverable and are called *plastic flow*.

To understand the mechanical properties of polymers we must examine the processes preceding their fracture and the mechanism of fracture.

9.1. DEFORMATION PROPERTIES OF POLYMERS

The mechanical properties of materials are usually studied by means of tensile testing machines or dynamometers. The stress versus strain dependence obtained with these machines is expressed by what is known as a *stress-strain curve*, the shape of which depends on the aggregation and phase states of the polymer tested.

During deformation the cross section of a specimen decreases. Therefore stresses may be calculated with respect to the original cross section S_0 or to the deformed cross section S at a given moment of time. The latter cross section is calculated by assuming that the volume remains constant during deformation, i.e., from the condition $S_0 l_0 = Sl$, where l_0 and l are the lengths of the undeformed and deformed specimens.

Hence,

$$\frac{S_0}{S} = \frac{l}{l_0} = \frac{l_0 + \Delta l}{l_0} = 1 + \varepsilon$$

and

$$S = \frac{S_0}{1 + \varepsilon} \tag{9.1}$$

where ε is the tensile strain.

The specimen breaks at a certain value of stress, which grows in the course of deformation.

The strength values obtained in this way are very high. In the case of solid polymers they lie between 500 and 1000 kgf/cm^2. However, mechanical strength is displayed only starting from a definite molecular mass. With increasing degree of polymerization the strength of a material first increases, and then becomes constant at $n = 600$. Figure 9.1 gives a general idea of the dependence of polymer strength on molecular mass.

Discontinuities can be caused in monomers and low-molecular polymers without applying large stresses.

Figure 7.3 (p. 186) is a typical stress-strain curve of a rubber-like polymer. The first portion of the curve corresponds to very small strains, which formally obey Hooke's law; on this portion the modulus is constant and not very large. The second portion of the curve corresponds to the development of rubber-like strain,

the nature of which is discussed in detail in Chap. 7; here the modulus of elasticity is of the order of 0,02 kgf/cm^2. On the third portion the modulus increases sharply, i.e., minor changes in strain cause big changes in stress. This is due to straightening of the chains and the change in their energy of interaction during strain (p. 187). At a definite stress value the specimen fails (point A).

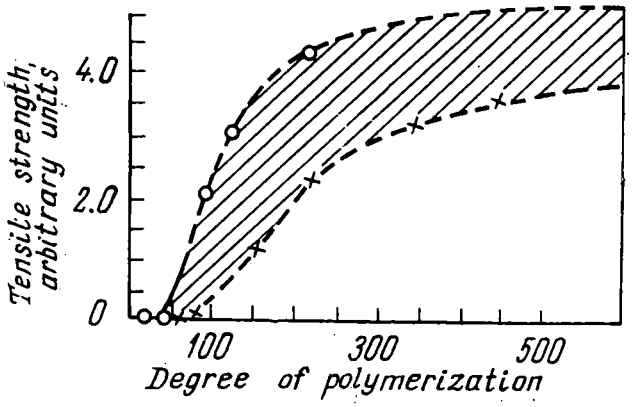


Fig. 9.1. Tensile strength versus degree of polymerization (circles — tensile strength of strongest polymers, crosses — of weakest polymers)

Thus, rupture of the specimen is preceded by very high recoverable deformations associated with molecular rearrangements. Hence, in this case rupture is not brittle. Bartenev suggested calling this kind of rupture *highly elastic.*

9.1.1. Glassy Polymers

Forced Elasticity. A characteristic feature of the glassy state of polymers is that small strain values correspond to low stresses. However, in contrast to simple low-molecular glasses (rosin, silicate glass, etc.), over a certain temperature interval glassy polymers retain the ability to respond to large stresses by considerable deformations, sometimes as high as hundreds of per cent. Macromolecular glasses often become brittle at temperatures scores of degrees below the glass-transition temperature. The ability of glassy polymers to deform considerably without breaking accounts for their wide usage in engineering.

For a long time it was thought that the considerable deformations caused by large stresses were due to flow processes, which were called "cold flow". However, flow, i.e., mutual displacement of macromolecules, is not very probable in the glassy state.

Aleksandrov and coworkers showed that a sample of poly(methyl methacrylate) which had a definite irrecoverable strain at a temperature below the glass-transition temperature recovered its ini-

tial shape and size after heating above T_g. The recoverable nature of the large deformations observed in high-molecular glasses suggests that the regularities of the rubber-like state apply to the glassy state as well. This is quite likely because glass transition is not a phase transition (Chap. 8) and a polymer possesses the same structure at temperatures above and below T_g. The only difference is that the relaxation time of a polymer in the glassy state is very great, and that is why a glassy polymer cannot be deformed greatly by applying comparatively small stresses.

According to Eq. (7.37) on p. 190, relaxation time depends on temperature and on the energy required for the molecules to rearrange themselves (activation energy). Aleksandrov suggested that the activation energy of molecular rearrangements is affected not only by the nature of polymer, but also by the magnitude of the stress applied, which lowers the activation energy, thus decreasing the relaxation time. To a first approximation the dependence of the relaxation time τ on the temperature T and stress σ is expressed by the equation

$$\tau = \tau_0 e^{\frac{\Delta U - \alpha\sigma}{kT}} \tag{9.2}$$

where α is a constant.

At small stresses, when $\alpha\sigma \ll \Delta U$, this equation becomes the same as Eq. (7.37) (p. 190), i.e., in this case the stress value does not affect the relaxation time. At large stresses τ becomes smaller and highly elastic strain appears.

Aleksandrov termed the large strains developing in glassy polymers only under the influence of considerable stresses, but close in nature to highly elastic strains, *forced elastic*, and the phenomenon *forced elasticity*.

As has already been indicated, forced elastic strains can appear only under high stresses. For this reason after the deforming stress is removed the rate of disappearance of forced elastic strains is very low, and they do not disappear at all at temperatures below T_g. At temperatures above T_g the specimen recovers its original size completely. Thus, the deformation of glassy polymers is always recoverable.

The process of deformation of glassy polymers, which is known as "cold drawing", has been studied in detail by Lazurkin.

Stress-Strain Dependence. In the course of deformation of many glassy polymers [polystyrene, poly(methyl methacrylate), poly(vinyl chloride), etc.], when a particular stress is reached, the specimen begins to extend nonuniformly (jumpwise). One part of the specimen becomes thinner than the rest and a neck is formed. Tensile strain accompanied by the formation of a neck is described, as a rule, by a curve of the kind shown in Fig. 9.2.

Some glassy polymers (e.g., cellulose acetate and nitrate) form no neck upon forced elastic deformation and then their stress-strain curves have no maximum (Fig. 9.3).

The ε vs. σ curve can be divided into several sections, characterizing the different stages of the deformation process.

The first region (*oa*) is a straight line representing strains formally obeying Hooke's law. In the region *ab* the slope of the curve decreases with increasing stress. This is connected with incipient development of forced elasticity in the specimen. With increasing stress the rate of development of forced elastic deformation increases rapidly, and this further decreases the slope of the

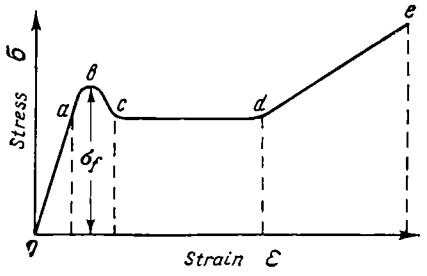


Fig. 9.2. The stress-strain curve of glassy polymers (involving neck formation)

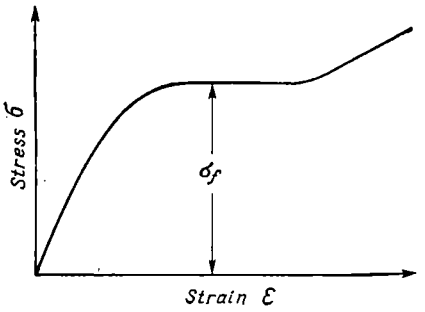


Fig. 9.3. The stress-strain curve of glassy polymers (not involving neck formation)

stress-strain curve. At the maximum (see Fig. 9.2) or in the plateau region (see Fig. 9.3) of stress-strain curves the tangent to the curve is horizontal, i.e., the rate of forced elastic deformation becomes equal to the total rate of deformation. The stress at which this occurs is called the *ultimate forced elasticity* σ_f. Near the maximum and in the region of declining stress is the point where necking starts. Neck formation is completed by the end of the stress drop.

The region *cd* — the part of the curve parallel to the abscissa — corresponds to elongation of the neck at the expense of the neighbouring, slightly deformed parts of the specimen ($\sigma = \text{const}$). At *d* the neck growth stops, i.e., the thickness of the entire specimen becomes equal to that of the neck. The region *de* corresponds to further deformation of the specimen at reduced cross section.

Forced elasticity, like high elasticity, depends on the rate of deformation, which is an indication of its relaxational nature. The higher the rate of deformation, the greater will be the stress needed to cause forced elasticity. This means that the ultimate forced elasticity rises with increasing straining rate. The follow-

ing empirical dependence can be derived between σ_f and the rate of deformation v:

$$\sigma_f = B + c \ln v \tag{9.3}$$

where B and c are constants.

Temperature Dependence of Ultimate Forced Elasticity. Brittle Temperature. Figures 9.4 and 9.5 are typical ε vs. σ curves for glassy polymers at different temperatures. It is evident from the figures that ultimate forced elasticity increases regularly with declining temperature.

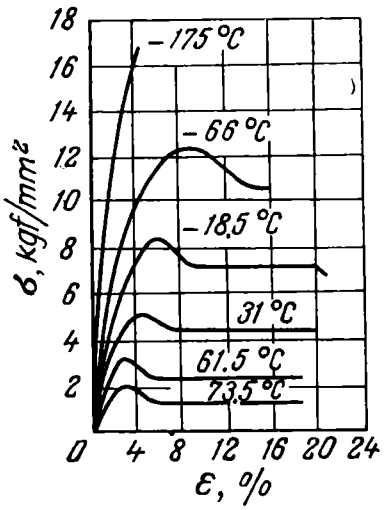


Fig. 9.4. Stress-strain curves for poly(vinyl chloride) at various temperatures

The temperature dependence of ultimate forced elasticity at different rates of deformation is illustrated by Fig. 9.6. It can be seen from this figure that the quantity σ_f depends not only on temperature but also on the rate of stress application, i.e., the relaxational nature of forced elasticity is evident. The σ_f vs. T line intersects the abscissa at a point corresponding to the glass-transition temperature of the polymer. At this temperature $\sigma_f = 0$; rubber-like deformation develops in the specimen already at low stresses.

The value of σ_f increases with declining temperature because the stresses required to regroup the chains become larger and larger. As long as the lifetime (p. 248) of the material under the stress in question is high, forced elastic deformation develops. At a certain fairly low temperature the stress required to regroup the chain sections corresponds to so short a lifetime that σ_f reaches the brittle strength value ($\sigma_f = \sigma_{br}$), and brittle fracture occurs. The temperature below which the polymer breaks under the action of this stress is called the *brittle temperature* (T_{br}). At the brittle temperature the ultimate forced elasticity is equal to the brittle strength.

The brittle temperature of a polymer can be determined graphically from the temperature dependence of brittle strength, i.e., the strength of a polymer on brittle fracture and of ultimate forced elasticity (Fig. 9.7). With increasing temperature the brittle strength of materials decreases somewhat, because at elevated temperatures cracks form and grow more intensively, and a smaller stress is required to cause failure.

Ultimate forced elasticity increases with declining temperature, the slope of the σ_f vs. T curve always being greater than that of

σ_{br} vs. T curve. The intersection of these two curves, at which $\sigma_f = \sigma_{br}$, determines the brittle temperature of the material *.

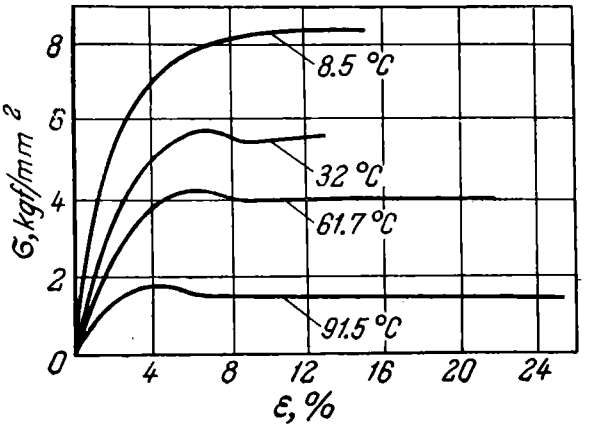


Fig. 9.5. Stress-strain curves for cellulose acetate at various temperatures

Note that the brittle temperature is still more conventional by its nature than the glass-transition temperature, because its location depends not only on the rate of loading, but on the kind of deformation (compression, extension, shear) as well.

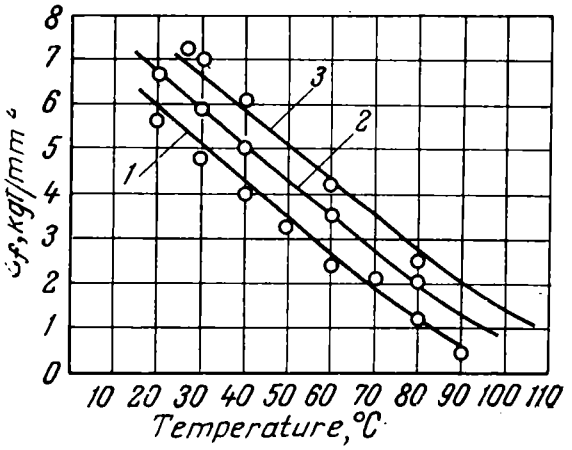


Fig. 9.6. Temperature dependence of ultimate forced elasticity of poly(methyl methacrylate) at various deformation rates:
$1 - v = 5.3 \times 10^{-5}$ s^{-1}; $2 - v = 5.3 \times 10^{-4}$ s^{-1};
$3 - v = 5.3 \times 10^{-3}$ s^{-1}

In the case of macromolecular glasses the brittle and glass-transition temperatures determined at equal deformation rates do not coincide (the former is always below the latter). The difference $T_g - T_{br}$ determines the temperature range of forced elasticity.

* In real polymers the temperature dependence of σ_f passes smoothly into that of σ_{br}.

If the upper temperature limit of serviceability of a plastic depends on the glass temperature, the brittle temperature determines its lower limit in many cases. Below this temperature large stresses will cause brittle failure of the polymer, Glassy polymers give the best performance in the temperature interval from T_g to T_{br}.

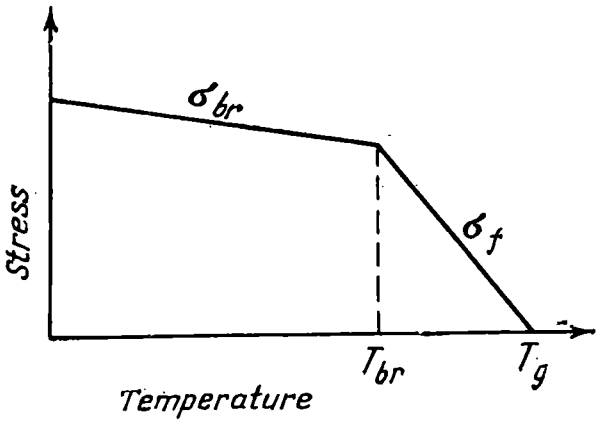


Fig. 9.7. Temperature dependence of brittle strength and ultimate forced elasticity

This makes a large temperature range of forced elasticity a very valuable property in a polymer.

TABLE 9.1. *Temperature Range of Forced Elasticity*

Polymer	T_g, °C	T_{br}, °C	$T_g - T_{br}$
Polystyrene	100	90	10
Poly(methyl methacrylate)			
initial	100	10	90
extended 100%	110	—50	160
Poly(vinyl chloride)	81	—90	171
Natural rubber, unfilled	—62	—80	18
СКБ *-base rubber, unfilled	—39	—112	73
СКС-30 *-base rubber, unfilled	—49	—135	86
СКН-40 *-base rubber, unfilled	—19	—110	91

* СКБ, СКС and СКН are Soviet code marks for butadiene, styrene and nitrile rubbers, respectively. The numbers following the code mark indicate the percentage of polystyrene in the copolymer.—*Tr.*

It is evident from Table 9.1 that the forced elasticity ranges of different polymers vary widely. Thus, poly(methyl methacrylate) has a much wider forced elasticity range than polystyrene, which predetermines its scope of application. A very large difference

between T_g and T_{br} is observed in poly(vinyl chloride). Rubbers lose their main service quality — high elasticity — at temperatures between —20 and —70 °C. Some rubbers (based on CKH-40 and CKC-30), however, retain a certain flexibility and the ability to undergo large deformations down to very low temperatures. At the same time, so frost-resistant a rubber as natural rubber has a very narrow forced elasticity range. Hence, articles to be used at very low temperatures should be made from CKH-40 rubber rather than from natural rubber.

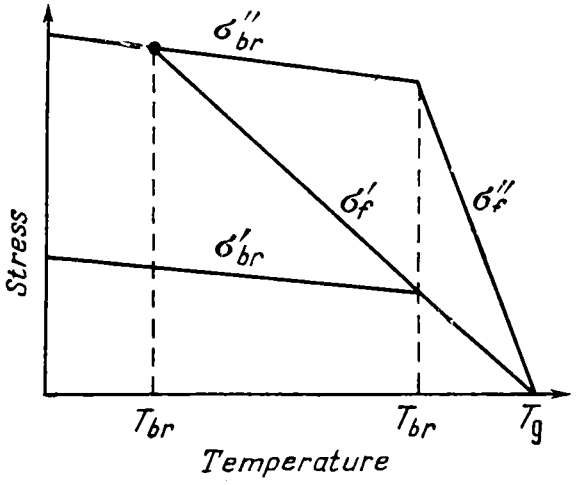


Fig. 9.8. Brittle temperature versus brittle strength and variation of ultimate forced elasticity with temperature

The forced elasticity range depends mainly on the value of the brittle temperature, which depends, in its turn, on the brittle strength of the material (σ_{br}) and on the nature of the temperature change of σ_f.

A high brittle temperature may be due to two causes: low brittle strength and sharp increase of the ultimate forced elasticity with decreasing temperature (Fig. 9.8).

The brittle strength of macromolecular compounds is usually very high, and hence, the latter factor becomes decisive: the sharper σ_f increases with decreasing temperature, the smaller will be the temperature range of forced elasticity.

The character of the temperature dependence of σ_f is determined by the nature of a polymer: its energy of intermolecular interaction, packing of its macromolecules, and its molecular mass.

Effect of Energy of Intermolecular Interaction. With increasing intermolecular interaction the temperature range of forced elasticity grows wider. This is due to the formation of strong bonds (cross-links) between the polar groups of the chains, which increases the brittle strength. At the same time these bonds are fairly labile and large stress may cause a regrouping of chain

sections to load the entire molecular network more uniformly. This means that forced elastic deformations may occur at lower temperatures and hence, the slope of the σ_f vs. T curve is small. It follows from Fig. 9.8 that in this case the brittle temperature will be low.

Effect of Packing of Macromolecules. The macromolecules of some polymers do not have time to form a dense packing during glass transition (Chap. 8). Loose packing of macromolecules facilitates changes in their conformation, i.e., favours the exhibition

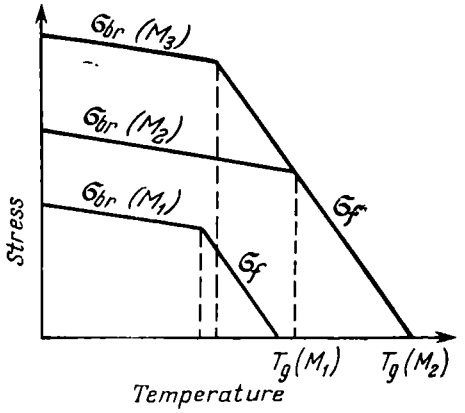


Fig. 9.9. Brittle strength and glass-transition temperature of polymers of different molecular masses ($M_3 > M_2 > M_1$)

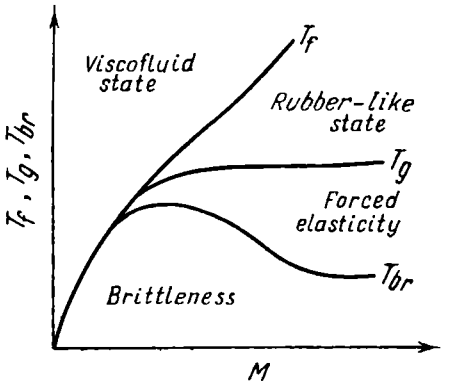


Fig. 9.10 Variation of flow, glass-transition and brittle temperatures with molecular mass of polymer

of forced elasticity on application of large stresses; then σ_f does not change very much on cooling (the σ_f vs. T curve has a gentle slope) and the brittle temperature is low. For example, the loose packing of macromolecules of cellulose nitrate and cellulose acetate causes a wide temperature range of forced elasticity.

Effect of Molecular Mass of a Polymer. In the high-molecular region the slope of σ_f vs. T is practically independent of molecular mass of a polymer, but the molecular mass affects the brittle strength and glass-transition temperature of the polymer. The glass temperature increases with molecular mass of a polymer up to a degree of polymerization of $n \approx 200$ (p. 220), and the brittle strength up to $n \approx 600$ (p. 234). Hence, with increasing degree of polymerization both T_g and σ_{br} increase up to $n = 200$ (from M_1 to M_2) so that the brittle temperature rises (Fig. 9.9).

With further increase of the degree of polymerization (from M_2 to M_3) T_g remains constant, but σ_{br} continues to increase, and therefore the brittle temperature declines. Beginning from a degree of polymerization of $n \approx 600$ the brittle temperature becomes constant.

Figure 9.10 shows the change in T_f, T_g and T_{br} depending on the molecular mass of a polymer. In low-molecular organic glassy compounds all three temperatures practically coincide. With increasing molecular mass the curves diverge. The flow temperature rises continuously with increasing molecular mass, while the glass-transition temperature first rises and then reaches a constant value (Chap. 8). The brittle temperature rises with increasing molecular mass, passes through a maximum and then falls off.

Above the flow temperature is the viscofluid region, between T_f and T_g is the region of the rubber-like state, between T_g and T_{br} is the region of forced elasticity, and below T_{br} the polymer is in the brittle state.

9.1.2. Crystalline Polymers

Crystalline polymers may undergo considerable deformations (up to 1000 per cent) under the action of a stress.

Many investigations have shown that a considerable part of these deformations are recoverable, i.e., they are forced elastic deformations by nature. As is the case with glassy polymers, a considerably reduced cross-sectional area, a neck, is suddenly formed in the sample of a crystalline polymer at a definite stress value.

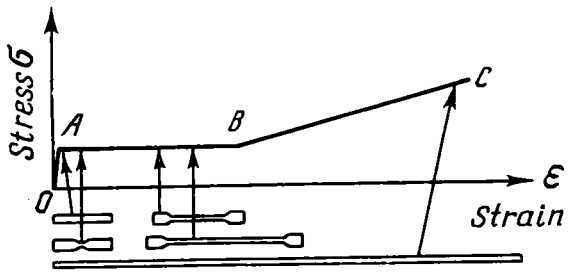


Fig. 9.11. Load-extension curve of a crystalline polymer at room temperature

The mechanical properties of crystalline polymers were studied in detail by Kargin and Sogolova. The stress versus strain (ε vs. σ) dependences of crystalline polymers are not smooth curves as in the case of the rubber-like or forced elastic states, but broken lines consisting of three portions (Fig. 9.11). Each of these portions corresponds to a definite physical process occurring in the strained crystalline polymer.

The portion OA corresponds to elastic strain, formally obeying Hooke's law, the sample stretching as a whole to a very small extent. The point A corresponds to the jumpwise beginning of neck formation.

The portion AB represents an increase in size of the narrow part of the specimen and a corresponding decrease of the wide part.

X-ray data show that at this stage of deformation the orientation of crystallites occurs in an initially isotropic specimen of a crystalline polymer at constant stress. If the initial specimen is anisotropic and is deformed in a direction perpendicular to that of the original orientation of its crystallites, re-orientation of the crystallites will occur on section *AB*. Orientation (or re-orientation) of crystallites begins at *A* and is completed at *B*, where the entire specimen has passed into the neck. Section *BC* corresponds to elongation of the re-oriented specimen as a whole, the deformation on this region being greater than on *OA*.

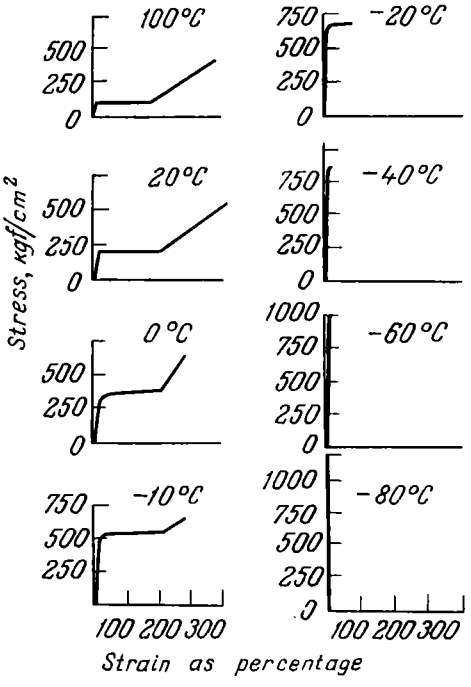


Fig. 9.12. Load-extension curves of isotropic crystalline polyamide at various temperatures

When an anisotropic crystalline polymer is deformed, the specimen possesses exactly the same structure and properties in the initial and final states. The only difference is that the directions of crystallite orientation in these states are at right angles.

Let us consider the effect of temperature on the mechanical properties of crystalline polymers, taking polyamide as an example. With decreasing temperature (below 25 °C) the horizontal plateau rises and the third region becomes shorter (Fig. 9.12). Hence, with decreasing temperature an increasingly higher stress is required to cause re-orientation; this will make fracture occur at smaller elongation. Further cooling raises the horizontal flat still higher and makes it shorter. This means that the specimen will fail upon incomplete re-orientation. At —60 °C the horizontal flat vanishes and only the first section remains. At temperatures from —70 to —80 °C the material becomes much stronger and entirely incapable of deforming in the direction perpendicular to the direction of orientation. At this temperature the specimen undergoes brittle fracture (p. 233) and breaks up into small fragments. In some cases at low temperatures a small maximum is observed on the σ vs. ε curves.

The stress at which neck formation begins and the fracture stress decrease with increasing temperature (above 20 °C), but the length of any region of the curve remains practically unchanged. The recrystallization stress decreases so much with increasing

temperature that at 216-218 °C (a temperature close to the melting temperature of polyamide crystallites) a small specimen will start to deform with necking under the action of a force equal to the specimen weight.

The above described regularities are observed for polyethylene, poly(vinylidene chloride), gutta-percha, crystalline rubber, polytetrafluoroethylene, polyamides and isotactic polystyrene. The absolute values of the stresses at which necking starts and of the fracture stresses at any temperatures depend on the type of a crystalline polymer.

Thus, the experimental material given above testifies to the fact that fracture of all polymeric materials is preceded by very large recoverable strains of a highly elastic or forced-elastic nature. Polymers break without preliminarily deforming, i.e., indergo brittle fracture only below the brittle temperature. In this case they completely lose their specific "polymeric properties".

9.2. EFFECT OF THE PRE-ORIENTATION OF CHAINS ON THE DEFORMATION PROPERTIES OF POLYMERS

One of the most common methods of changing the structure of a polymeric material to strengthen it is by drawing it during processing. This orients its chains and supermolecular structures. If the polymer is an amorphous one with molecules of regular structure, it may even crystallize.

A pre-oriented elongated sample of a polymer displays anisotropy of mechanical properties in a test, i.e., the fracture stress for deformation in the direction of orientation is very high, much higher than in an unoriented sample or than in the direction perpendicular to orientation in an oriented sample. On the other hand, the elongation per unit length of an oriented sample in the direction of orientation is always smaller than in the direction at right angles to it. This is due to the fact that pre-stretched chains possess less flexibility and are therefore less capable of straightening.

Thus, the mechanical properties of oriented polymers are anisotropic, this being due to orientation of their chains. Anisotropy appears in polymeric materials in the process of fabrication (e.g., during calendering). A calendered material is always stronger in the direction of calendering than in the direction perpendicular to it (*calender effect*). Anisotropy is also observed in cold-drawn polymeric materials.

Pre-orientation of glassy polymers broadens their temperature range of forced elasticity. This is related to the fact that orientation increases their brittle strength more than their ultimate forced elasticity, and therefore lowers their brittle temperature. Since

orientation has practically no effect on the glass-transition temperature, decreasing the brittle temperature increases the temperature interval of forced elasticity. For example, the forced elasticity temperature range of unoriented poly(methyl methacrylate) is 100 °C, and that of a sample pre-stretched 100 per cent is 160 °C (see Table 9.1).

Orientation has a considerable effect on the mechanical properties of crystalline polymers. Figure 9.13 contains stress-strain curves of pre-oriented polyamide tested in the direction of

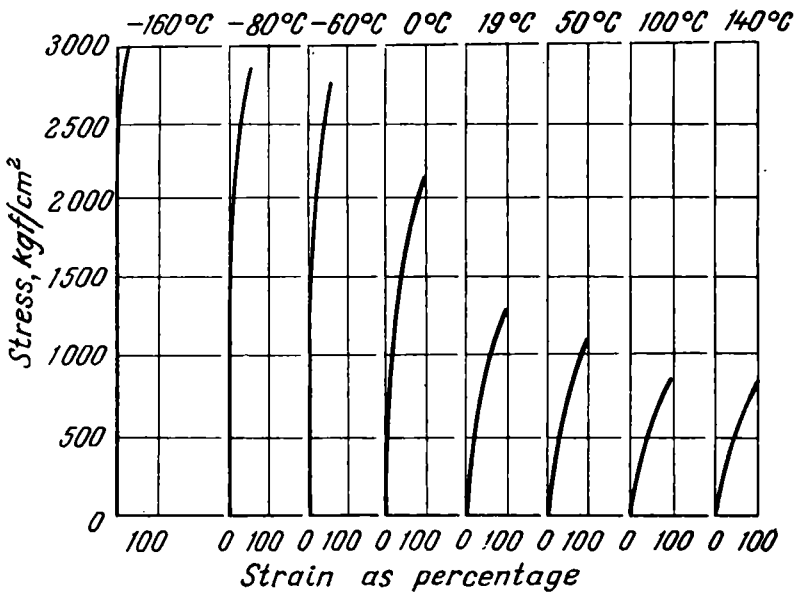


Fig. 9.13. Tensile stress-strain curves of oriented polyamide extended in the direction of orientation at various temperatures

orientation. It is evident from the figure that in the direction of orientation the tensile strength of oriented crystalline polymers is higher, and their elongation per unit length is much smaller than in the direction perpendicular to orientation (see p. 244). With decreasing temperature the strain decreases and the tensile strength increases regularly.

When highly oriented crystalline polymers are being deformed, only elastic deformation is exhibited, i.e., they are fractured brittly. However, their fracture greatly differs from what unoriented polymers undergo at low temperature, when they disintegrate into small pieces. Such a phenomenon is alien to oriented polymers even at low temperature.

Orientational strengthening of polymers may occur not only during fabrication but also during deformation. This is observed when polymers in the elastic state are stretched. The strength of such polymers is mainly due to their ability to crystallize. Thus,

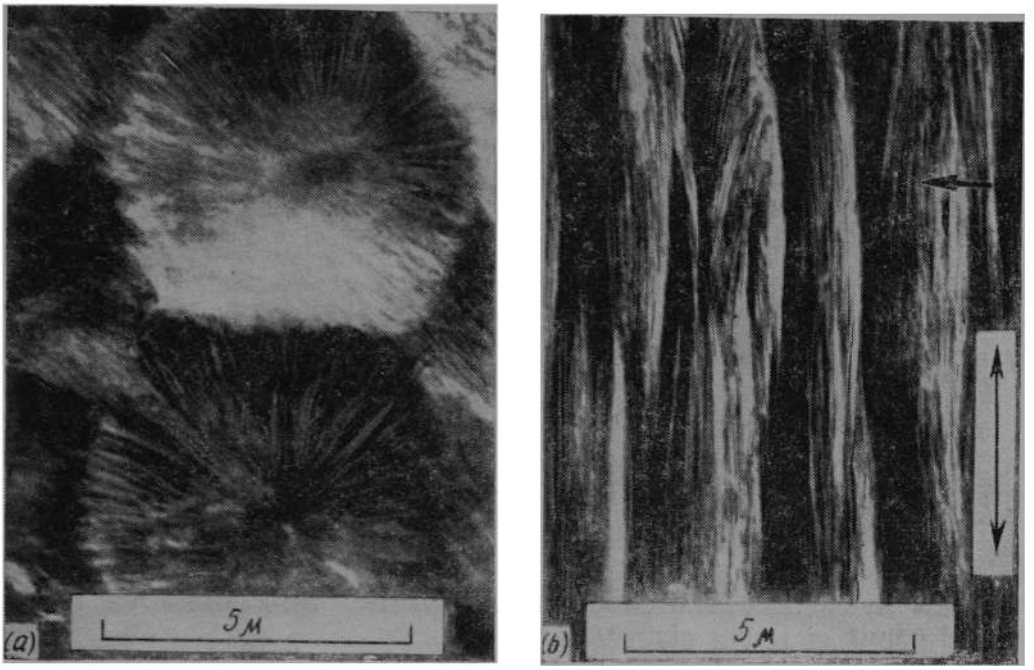


Fig. 9.14. Effect of orientation on spherulite shape:
a—unoriented polycaproamide sample; *b*—230 per cent elongation

there are rubbers which are very strong even in an unfilled state, and others which are very weak though some of them contain polar groups in their chains (Table 9.2). Rubbers of group I crystallize when extended; those of group II do not.

TABLE 9.2. *Tensile Strength of the Vulcanizates of Rubber-like Polymers*

Group I		Group II	
Polymer	Tensile strength, kgf/cm²	Polymer	Tensile strength, kgf/cm²
Natural rubber	300	Rubber СКБ	10
Polychloroprene	270	Rubber СКН-26	10
Butyl rubber	200	Rubber СКС-30	14

It is interesting to note that elastic fibres are not made from rubber-like, but from solid polymers containing groups capable of strong intermolecular interaction, such as polyamides. The presence of such groups ensures a wide temperature range of forced elasticity.

Orientation of a polymer involves not only straightening of its chains, but also a rearrangement of supermolecular structures.

Thus, slow stretching of polycaproamide films changes the shape of their spherulites. The symmetrical spherulites in the initial sample (Fig. 9.14*a*) change into formations of a fibrillar nature drawn out along the extension axis (Fig. 9.14*b*).

9.3. MECHANICAL STRENGTH AND LIFETIME OF POLYMERS

Strength is the ability of a body to withstand a load without breaking. Strength is usually characterized by the stress which causes failure. This stress is called the *fracture stress* or *tensile strength* and is expressed in kgf/cm^2 or kgf/mm^2.

The tensile strength of a material is determined, as a rule, from its stress-strain curves. It is the limiting stress at which the specimen fractures. This definition is generally accepted and one usually speaks of *ultimate strength.*

For a long time it was thought that discontinuities of materials (tear or cleavage) occur when the stress (normal or shear) reaches a certain critical limiting value, and that no failure would occur at lower stresses.

At present it has been established that this conception of failure is incorrect, because all materials fail, if subjected to prolonged loading, at stresses much below those that arise upon fast application of the load. This means that the tensile strength depends on the time of loading.

The time dependence of strength under static load is called the *static fatigue*, and the time dependence of strength under dynamic load, the *dynamic fatigue* of a material. Both these phenomena are often called *endurance.*

Static and dynamic fatigue is observed during the deformation of metals, silicate glasses, plastics, fibres, rubbers, and other materials.

In this connection, the concept of lifetime of material was introduced. *Lifetime* is the time between the moment when force is applied and the moment when the material is ruptured. This is a fundamental characteristic of the strength properties of all materials. A study of the dependence of lifetime on test conditions sheds light on the physical nature of fracture. Knowledge of the lifetime of materials, including polymeric materials, is needed for making engineering calculations for the strength of constructions and parts.

The strength versus time dependence of polymers was investigated in detail by Zhurkov, who studied the lifetime of polymeric materials under static load.

The fracture stress was selected so that the lifetime of the materials studied should vary over 5 to 10 orders of magnitude. The results obtained are shown in Fig. 9.15, from which it follows that

the stress dependence of the logarithmic lifetime τ is a straight line:

$$\tau = Ae^{-\alpha\sigma} \tag{9.4}$$

where σ = stress
A and α = constants depending on the kind of material.

Note that the dependence shown in Fig. 9.15 becomes invalid as σ approaches zero, otherwise it would indicate the absurd situation that a body could exist for only a limited time in the absence of load. Experiment shows that with σ tending to zero the

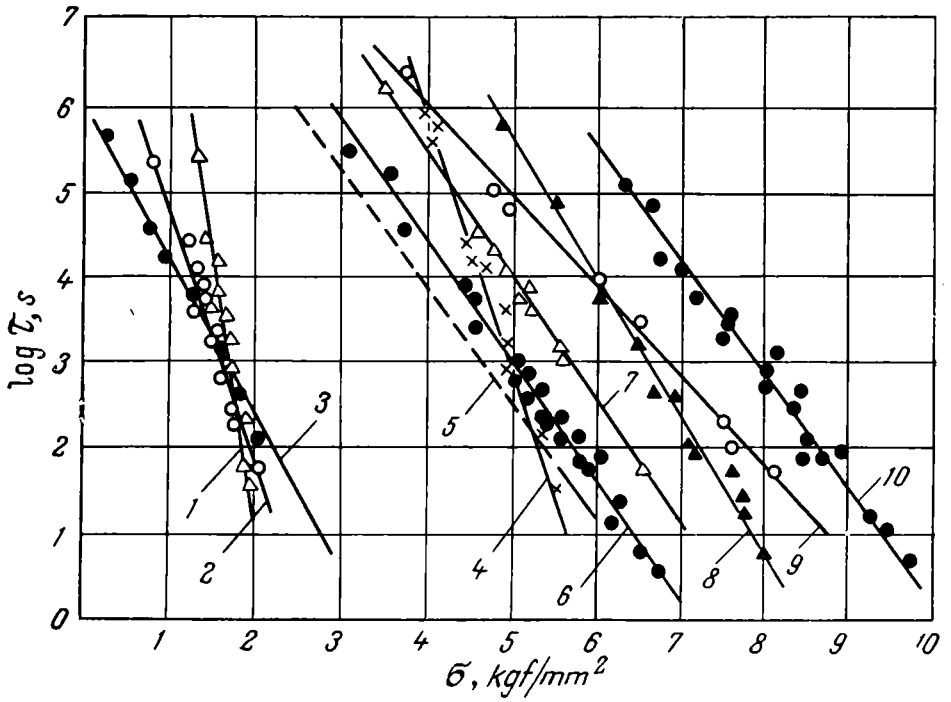


Fig. 9.15. Plots of lifetime against stress:
1—rubber without carbon black (Buna S); *2*—vinyl blend [poly(vinyl chloride)]; *3*—rubber without carbon black (Buna N); *4*—aluminium foil; *5*—plexiglas; *6*—polystyrene; *7*—cellophane; *8*—celluloid; *9*—cellulose acetate; *10*—cellulose nitrate

straight line becomes a curve asymptotically approaching the ordinate axis. However, for a very wide range of stresses the log τ vs. σ dependence remains linear.

This kind of dependence of lifetime on stress is observed over a wide temperature interval (Fig. 9.16). The lower the temperature, the larger the slope of the line, i.e., the greater the values of A and α. It follows from Fig. 9.16 that at fairly low temperatures the log τ vs. σ dependence is represented by a very steep line, i.e., minor changes of σ result in astronomic values of log τ or make this value very small, giving the impression of instantaneous fracture. This makes it easy to understand how the concept of critical failure and ultimate strength appeared.

Such a temperature-time nature of dependence of strength is sufficiently universal; straight lines converge on a point called the *pole*, whose ordinate is $\log \tau_0 = -12$, i.e., $\tau_0 = 10^{-12}$ s.

A study of the temperature-time dependence of the strength of solid polymers led to the discovery of the relation between the

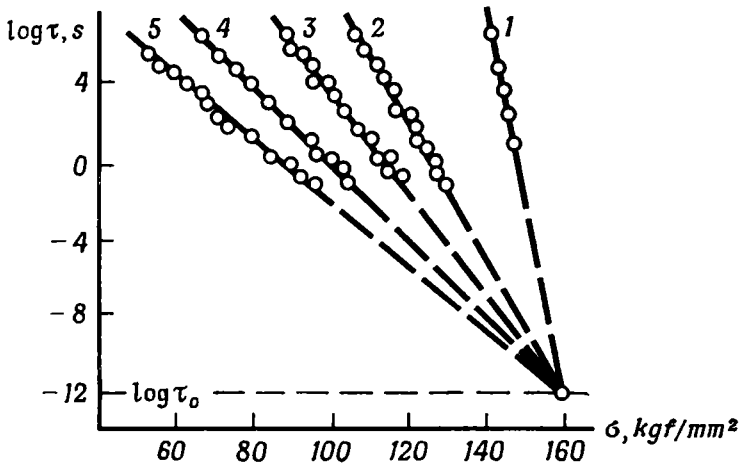


Fig. 9.16. Dependence of lifetime on stress for capron at various temperatures: *1*— −180 °C; *2*— −120 °C; *3*— −75 °C; *4*— −20 °C; *5*— −80 °C

breaking stress σ, the lifetime of a polymer under the load τ and the absolute temperature T. This dependence is represented by the equation

$$\tau = \tau_0 e^{\frac{U_0 - \gamma\sigma}{kT}} \tag{9.5}$$

where k = Boltzmann constant

U_0, γ, and τ_0 = parameters determining the strength properties of the polymeric material.

Equation (9.5) is known as the Zhurkov equation. It reduces to Eq. (9.4) at $A = \tau_0 e^{U_0/kT}$ and $\alpha = \gamma/kT$.

Equation (9.5) is not merely an empirical relation, but possesses profound physical sense, which becomes obvious if it is compared with the fundamental Boltzmann-Frenkel equation

$$t_{\text{eff}} \approx \frac{1}{\nu_0} e^{\Delta U/kT} \tag{9.6}$$

where t_{eff} = effective time of occurrence of any activation processes, i.e., processes in which the atoms have to overcome activation barriers *

* We encountered such processes when examining internal rotation in molecules (Chap. 4) and rubber-like deformation (Chap. 7). Other activation processes are viscous flow (Chaps. 8 and 10), dielectric polarization (Chap. 11), diffusion (Chap. 21), etc.

ν_0 = frequency of thermal vibrations of the atoms in the solid about their equilibrium positions, equal to 10^{13} vibrations per second

kT = average energy of such thermal vibrations

ΔU = potential or activation barrier, depending on interatomic interaction.

It is quite obvious that not all atoms can overcome the activation barriers, but only those of them whose $kT < \Delta U$, i.e., atoms possessing excess kinetic energy, or "fluctuation energy", due to the inevitably nonuniform distribution of energy among atoms.

For most solids, including the majority of polymers, $\tau_0 = 10^{-12}$-10^{-13} s. This is not by chance, since τ_0 is a quantity inverse to ν_0, i.e., it is the time of thermal vibrations of atoms in solids. If this is so, the quantity $U_0 - \gamma\sigma = \Delta U$ is the effective potential barrier determining the rate of fracture of a solid polymer, and the fracture itself is a typical activation process, occurring in time.

The value of the effective activation barrier ΔU can easily be determined. For this purpose the lifetime versus fracture stress dependence at different temperatures is studied. Presented as the dependence of logarithmic lifetime on inverse temperature, these data form a series of lines which converge upon extrapolation at a pole, situated on the ordinate axis (Fig. 9.17). The equation of these lines can evidently be obtained by taking the logarithm of Eq. (9.5):

$$\log \tau = \log \tau_0 + \frac{U_0 - \gamma\sigma}{2.303k} \cdot \frac{1}{T} \tag{9.7}$$

Hence, $\log \tau_0$ is the intercept of the lines on the ordinate axis.

It follows from the relation

$$\Delta U = U_0 - \gamma\sigma \tag{9.8}$$

that the dependence of ΔU on the fracture stress should be a straight line, the ordinate intercept of which is U_0, and the slope to the abscissa axis, γ. In this way the strength parameters of a polymer U_0 and γ can be determined from the experimental lifetime versus temperature and stress dependence.

U_0 is the *initial activation barrier*, from the value of which one can judge which bonds will break upon deformation of the body.

The physical sense of this quantity will be clear from the following reasoning: $\gamma\sigma$ is the part of the work done by the external forces in breaking the body. Assuming that rupture between the atoms occurs when the distance between their centres is doubled (when they are moved apart to a distance equal to an atomic diameter l), the work done by the external force in tearing two atoms

apart equals

$$\gamma\sigma = f_\alpha l \tag{9.9}$$

where f_α is the force acting on each atom.

If the load were distributed uniformly among the atoms in the cross section, the force per atom would approximately be σl^2. Then

$$\gamma \approx l^3 \approx V_\alpha \tag{9.10}$$

where V_α is the volume of an atom, equal approximately to 10^{-23} cm^3.

Indeed, the quantity γ has the dimension of volume (U_0 is expressed in dyne-cm, and the quantity σ, in dyne/cm^2). But for various materials γ is tens and hundreds of times larger than the

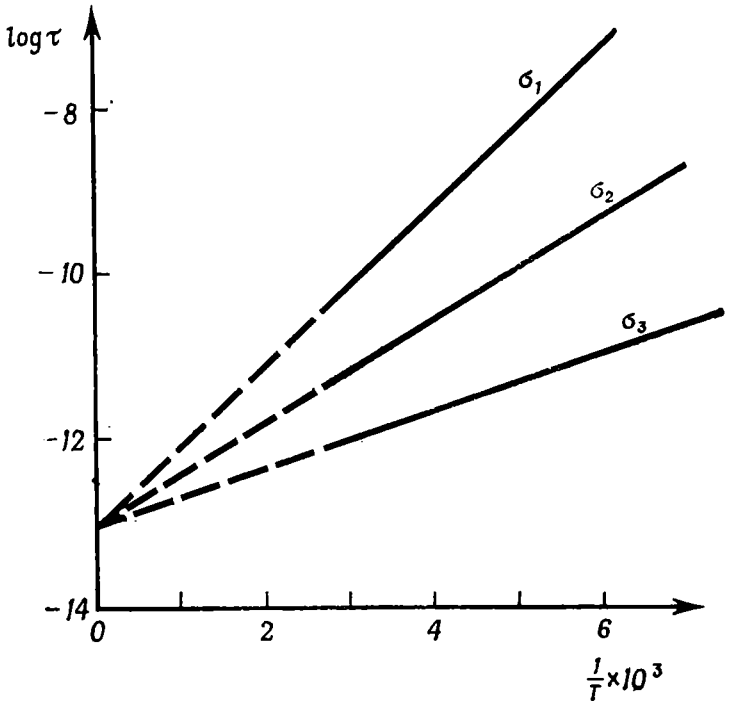


Fig. 9.17. Dependence of lifetime on inverse temperature at various rupture stresses

value of V_α. This means that the load is not uniformly distributed in the material. Evidently, at the point where fracture occurs the acting load is much greater than the average stress in the body. In this connection the ratio γ/V_α can be regarded as the "overstress coefficient". Such overstresses may occur due to nonuniformities which always exist in real solids. These nonuniformities are much larger in size than atoms and their immediate vicinity, i.e., they belong to the category of superatomic and supermolecular structures.

Hence, γ is a parameter which characterizes the structure of a body. Many works show that its value changes as the structure of a body changes, for example, in the case of annealing, orientation, plasticization (p. 265), and so forth. Therefore, the parameter γ is known as the *structure-sensitive parameter*. The more perfect the structure of a body and the more uniform the load distributed in it, the smaller is the magnitude of γ and the higher is the strength, which according to Eq. (9.5) can be expressed as follows:

$$\sigma = \frac{U_0}{\gamma}\left(1 - \frac{kT}{U_0}\ln\frac{\tau}{\tau_0}\right) \tag{9.11}$$

The Zhurkov equation is valid for many polymers. However, deviations from Eq. (9.5) are observed when the ranges of temperatures and stresses grow and especially when polymers which change their structure in the course of deformation are being tested. These deviations are expressed in pole displacement and in the divergence of the value τ_0 from the values of 10^{-12}-10^{-13} s. In some cases, the dependence of log τ on σ is expressed not by straight lines, but by curves. In particular, Eq. (9.5) is invalid for rubbers; in this case, the Bartenev equation fits better,

$$\tau = B\sigma^{-b} \tag{9.12}$$

where B and b are constants.

The temperature dependence of the strength of rubbers is represented by the empirical equation

$$\tau = C\sigma^{-b}e^{U_0/RT} \tag{9.13}$$

where U_0 and C are constants depending on the chemical constitution of the rubber and the structure of the vulcanizate.

In the case of rubbers, in contrast to solids, the stress has practically no effect on the energy U_0, but changes the value of the preexponential term. The value of U_0 for CKC-30-base rubbers, for instance, is 13.2 kcal/mole. The low values of this energy are evidence of the fact that the kinetics of fracture of rubbers depends not only on chemical but on intermolecular bonds as well.

All these points to the temporal nature of the strength of polymeric materials, and such concepts as ultimate strength, fracture stress, etc., become arbitrary. One cannot state the load a polymer can withstand without indicating the time during which the sample will resist fracture.

One might naturally ask: what is the breaking stress measured during conventional tests of polymers on tensile testing machines? During the test the stress in the sample gradually increases, and hence, according to Eq. (9.4), the lifetime decreases exponentially. When the lifetime τ of the material becomes commensurable with the duration of the experiment, the sample fails.

9.4. THERMAL FLUCTUATIONAL NATURE OF FRACTURE. NATURE OF RUPTURING BONDS

A systematic study of the lifetime of materials which differ from one another by their structure and properties, and the determination of the strength parameters U_0, τ_0 and γ, have made it possible to develop the conception of the kinetic nature of fracture and the thermal fluctuation theory of strength. The dependence of lifetime on stress clearly shows that fracture is a process which occurs in time, i.e., it proceeds at a definite rate, and lifetime can be regarded as a quantity inversely proportional to the average rate v of the fracture process. Moreover, it follows from the Zhurkov equation that the lifetime of a body likewise depends on stress and temperature: both parameters are in the exponent. Hence the assumption that thermal energy and precisely its fluctuation are very important in the fracture process, i.e., in the place of a material where thermal fluctuations become greater than the bond being ruptured, the latter is broken. Stress makes it possible for these fluctuations to accumulate in a definite direction and reduces the activation energy of rupture.

One of the basic points in this conception is the nature of the bonds being ruptured. In the case of rupture of atomic or ionic crystals, the bonds between atoms or ions are ruptured when these crystals are being fractured. There are two types of bonds in polymers, chemical and intermolecular ones, which differ from one another by length and energy (p. 45). Which of them are ruptured when the polymer is being loaded? This may be determined by the values of strength parameters.

According to the Zhurkov equation, the parameter U_0 is the initial activation energy of rupture. The values of U_0 determined from experiments in lifetime (p. 251) for many polymers are equal to 30-50 kcal/mole and approach the activation energy of chemical reactions (p. 49). In addition, their values in many cases do not depend on structural changes in the polymer, which should necessarily affect intermolecular interaction. Hence, Zhurkov and his co-workers assumed that it is precisely the chemical bonds which are ruptured when the polymer is being loaded. According to their hypothesis, these bonds become strained under the action of stress, and strained bonds burst under the action of thermal fluctuations. This hypothesis has been proved for uniaxially oriented polymers, when chemical bonds are arranged in one direction. Various physical methods have been used to prove this.

For example, polymer sample was under a load directly in the chamber of an infrared spectrometer. In this case, frequency shift was observed, indicating the elongation of the C—C bonds which occurs under the action of stress.

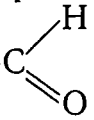
The method of electron paramagnetic resonance was used, and the sample was loaded in the chamber of the EPR-spectrometer. Free radicals were detected, and this was direct proof of the rupture of chemical covalent bonds. The intensity of the EPR signal was used to study the rate of accumulation of radicals as dependent on stress, temperature and time; this rate turned out to be in direct proportion to the stress and lifetime of these samples which was measured by independent method.

These experiments irrefutably prove that chemical bonds burst in oriented polymers when they are stretched.

Proof of the fact that rupture is caused by thermal fluctuations was given in Regel's works. Polymer samples were loaded directly in the mass spectrometer. It was discovered that the mass spectra of volatile products isolated in the course of loading at ordinary temperature were identical to the spectra obtained when the samples of these polymers were heated. These experiments show that loading causes processes characteristic of thermal degradation, which is undoubtedly a thermal fluctuation process. It turned out that, for many polymers, the magnitudes of the activation energy of thermal degradation satisfactorily conform to the activation energy of rupture (Table 9.3).

TABLE 9.3. *Activation Energies of Fracture and Thermal Degradation*

Polymer	Activation energy of fracture U_0 (kcal/mole)	Activation energy of thermal degradation (kcal/mole)
Polycaproamide	45	43
Cellulose triacetate	49	45
Polyethylene	25	20-25
Cellulose nitrate	38	38
Polystyrene	33	35
Poly(methyl methacrylate)	31	30

In the spectra of loaded polymers, Novak and Vetegren detected frequencies corresponding to oxidized groups, particularly the aldehyde groups  . These groups appear owing to the great reactivity of free radicals which are formed at the ends of the ruptured chains, these radicals are readily oxidized in air. These results have enabled Zhurkov and Korsukov to regard the mechanical fracture of the polymer as a mechano-chemical reaction whose rate is determined by the same parameters usually used in studying chemical reaction rates.

But what about the role of intermolecular bonds in polymer fracture? They are very important especially in orientation processes and, strictly speaking, they are the ones that determine the higher strength of oriented polymers.

In orientation, macromolecules are arranged practically parallel to one another, and therefore intermolecular bonds are summed up along the length of macromolecules. Since there are very many of them, the total interchain interaction grows very sharply and becomes commensurable with the chemical bond energy. To tear the sample of an oriented polymer, it is necessary to immediately rupture many chemical bonds, and this requires great loads.

In orientation, the structure-sensitive coefficient γ diminishes, and thus a material becomes stronger [Eq. (9.11)]. The values of U_0 and τ_0 do not change in this case. The greater the interchain interaction, or the cohesion energy (p. 162), the smaller is γ and the higher is the strength.

Since intermolecular interaction depends on the nature of atoms and distances between them, polymer strength depends on both factors. The effect of distance between molecules can be demonstrated by the following example: a cellulose molecule contains very many polar OH groups, but very high strength is not attained when cellulose fibres are being oriented, because sufficiently rigid macromolecules cannot be densely packed. Conversely, macromolecules of nonpolar polypropylene, being very flexible, are packed considerably more densely in orientation, and crystallization occurs. Therefore, polypropylene fibres are stronger than cellulose ones. Orientation of polymers of the former type results in what is known as "steel-like" fibres whose strength (ca. 120 kgf/mm^2) may be as high as that of some grades of steel. Taking into account that the density of a polymer is approximately one eighth that of steel, the strength of the polymer calculated per unit mass is now already four times that of steel.

There should be great interchain interaction in aromatic polymer molecules, and therefore high-strength thermostable fibres are made of aromatic polyamides. Table 9.4 gives the strength values of some fibres.

Intermolecular interaction is exhibited when nonoriented polymers, especially polymers in a rubber-like state, are being fractured. In these cases, as we have already seen, fracture is preceded by great recoverable deformations, and flow processes may occur in the rubber-like state. Flow processes can cause a part of the sample to slip, and then intermolecular bonds are ruptured. The fracture of such materials is a more complicated process, being accompanied with deformation processes (in the course of which macromolecules are straightened out and the structure changes) and with fracture processes. Undoubtedly, in this case, both chem-

TABLE 9.4. *Strength of Fibres*

Fibre	Tensile strength, kgf/cm²	Fibre	Tensile strength, kgf/cm²
Flax	6000-10 000	Natural silk	3000-5000
Cotton	2300-4500	Natural wool	1500-1900
Rayon fibre		Chlorinated poly(vinyl	
unoriented	1600-3000	chloride) fibre . . .	2900-4000
oriented	up to 7800	Nylon (Capron)	5000-7200
Acetate fibre		Terylene (Lavsan) . . .	5200-8000
unoriented	1600-1800	Orlon (Nitron)	2000-4000
oriented	up to 6000	Polyethylene fibre . .	1200-2000
		Steel (for comparison)	5000-20 000

ical and intermolecular bonds are ruptured, and separate sections of the ruptured chains are displaced; after displacement, these sections may recombine with one another into linear macromolecules or spatial networks. These processes need to be studied on the molecular level just as thoroughly as it was done with highly oriented polymers.

9.4.1. Mechanism of Polymer Fracture

Many researchers have tried to calculate the strength of solids on the basis of the forces of interaction between particles of a body (atoms, ions). Calculated strength is known as theoretical strength, which differs from the experimentally found (technical) strength. For real solids, the calculated strength is greater than technical strength by about two orders. To explain this, Griffiths proposed the hypothesis of the effect of surface cracks on the strength of real bodies. That the ideas of the hypothesis are sound was shown by Ioffe and his pupils. They ruptured rock salt specimens simultaneously dissolving their surface layer which contained cracks, and found that this increased the fracture stress from 0.4 to 150 kgf/mm². It is known that glass filaments pickled preliminarily with fluoric acid to remove their surface layer also become much stronger.

When polymeric articles are subjected to mechanical action, cracking or crazing occurs, usually starting at the most stressed point, e.g., at the holes by which the parts are fastened. Crazing is especially harmful in the case of polymers used in fields where optical properties are important, as these are deteriorated by crazing. The cracks reflect and scatter light, making the surface turbid or "silvering" it. If such parts are examined at a certain angle, the surface shows a bright lustre.

Cracking may be caused by external or internal stresses. Internal stresses are stresses arising during fabrication of the sample and balancing each other inside it. Sometimes cracking occurs in a polymer only under the action of such internal stresses. For example, a polystyrene sample with internal stresses will crack if immersed in a solvent or upon subsequent evaporation of that solvent.

By observing the formation and growth of surface cracks in polymers under a microscope it was established that the cracks do not arise instantaneously after the load is applied, but after some time. Then new cracks form, and those that appeared earlier gradually grow larger. Therefore, a sample contains cracks of a great variety of sizes. The rate of their appearance (the number of cracks appearing per 1 cm^2 of surface area per 1 s) and their rate of growth (increase of the length of a crack visible under the microscope per 1 s) depend on stress and temperature. The rates of both processes increase with increasing temperature and increasing stress. After a certain limit is reached the number of cracks ceases to grow, but their size continues to increase.

Crazing may occur not only on the surface but throughout the bulk, and it is an irreversible process. Prolonged rest of the sample after removal of the load decreases the size of the crack but does not heal it entirely. The crack remains and begins to grow again as soon as any tensile force is applied.

Within a certain temperature interval deformation of transparent glassy polymers causes whitening at the point of neck formation. This is related to the formation of the microcracks. The higher the temperature of deformation, the weaker will be the whitening, and near T_g it vanishes entirely.

Microcracks also arise in samples which do not form necks when extended, but in this case crack formation is less intensive.

If extension of a glass polymer is stopped long before fracture occurs, and the specimen is heated to a temperature above T_g and cooled again to the initial temperature and again strained, the polymer will be found to possess the same mechanical properties as in the first case (before heating). Evidently, small strains do not cause microcracks to form or cause very small ones.

When polymer samples are extended to fracture, or almost to fracture, macroscopic cracks appear, which do not heal when heated above T_g. Even if after annealing these cracks become so small as to be invisible under the microscope, the material will crack anyway afterwards during the experiment. Hence, these changes in mechanical properties are irreversible.

Cracking in polymers depends largely on the method of their processing. It is caused mostly by the tensile stresses remaining in the material after extrusion or other technological operations.

Thus, if a polystyrene sample, in the surface layer of which tensile stresses are acting, is immersed in a solvent, it will crack, but if compressive stresses are operating in its surface layer, it will not crack under the same conditions. Preliminary annealing always increases the resistance of a polymer to cracking.

The fluctuation theory of strength and the experimental data given in the previous section offer a good explanation of the cause of formation of microcracks and the mechanism of polymer fracture.

The initial act of fracture is the strain of the chemical bond. The strained bond bursts under the action of thermal fluctuations. There are comparatively few such overstressed bonds, but they are determinative in the fracture process. In crystalline polymers, they originate in amorphous regions on the so-called tie molecules (p. 120). This has been proven by the method of X-ray small-angle diffraction. It is in these regions, where macromolecules are mainly ruptured, that *nuclei of cracks* or *submicroscopic*, i.e., cracks ranging from 10 to 10^4 Å, originate. These cracks are disc-like and are perpendicular to the loading axis. They originate only under a load and do not heal after the load is removed. Submicroscopic cracks have been detected by the method of X-ray small-angle diffraction and by the scattering of visible light not only in oriented crystalline polymers, but also in amorphous ones. After they are formed, they may merge, producing larger *microcracks*, which are detected when the surface of a loaded polymer is examined under light microscopes. In the course of time, open *main* cracks, being the largest ones, begin to be formed, and their growth rate sharply increases with growing stress. At the tops of these cracks, the stress is considerably greater than its mean value. As a result of such an overstress, the sample bursts.

9.5. EFFECT OF VARIOUS FACTORS ON THE MECHANICAL PROPERTIES OF POLYMERS

Mechanical properties of polymers depend not only on the phase state and degree of orientation, but also on several other factors: the size and shape of supermolecular structures, the content and nature of the filler, and the crosslink density of the spatial network.

9.5.1. Effect of Size and Shape of Supermolecular Structure on Polymer Strength

The size and shape of supermolecular structure have a major effect on the mechanical properties of a polymer. For example, heating polypropylene for different periods of time results in

samples with spherulites of different sizes. Changing the structure of a polymer can simultaneously increase its strength and ability to undergo rubber-like deformation. Crystalline polymers may possess very good elastic properties; e.g., the elongation of polypropylene may be as high as 900 per cent, and its strength 370 kgf/cm^2.

The strength of polymeric materials is also greatly affected by the shape of their supermolecular structures. By altering synthesis conditions, Slonimsky, Korshak, Vinogradova and coworkers produced the polyester of isophthalic acid and phenolphthalein in the fibrillar and globular forms. The mechanical properties of these samples differed greatly. Thus, the impact strength * of the fibrillar sample was 6-10 kgf·cm/cm^2, and of the globular one — 2-3 kgf·cm/cm^2. Polymers of globular structure are brittle as a rule and break under impact.

Thus, the mechanical properties of polymers can be changed considerably by merely changing their structure.

9.5.2. Effect of Fillers on Mechanical Properties

The addition of fillers to a polymer to improve the properties of the finished articles has been practised for a very long time (especially in the production of technical rubber goods). Fillers which increase mechanical strength are called active fillers, and those that do not, are called inactive. The action of active fillers (carbon black and silica gel) is especially strong in СКБ, СКН and other rubbers. Fillers increase the strength of cured rubbers based on these rubbers by 10 to 20 times.

An active filler will sharply enhance the tensile strength of rubbers based on synthetic elastomers in the rubber-like state (СКБ, СКС-30, etc.). The effect of the filler on the properties of rubbers in the glassy state is the opposite. Thus, at temperatures where СКБ elastomer is in the elastic state the strength of the unfilled rubber based on it is 14 kgf/cm^2 and that of the filled rubber (60 parts by weight of furnace black) is 170 kgf/cm^2. Below the glass-transition temperature addition of a filler somewhat increases the value of σ_f and the brittle strength of the rubber decreases. The brittle temperature rises by about 41 °C. If the range of forced elasticity is 73 °C without filler, it narrows down to 32 °C when filler is added. Addition of filler has a similar effect on a rubber based on butadiene-styrene elastomer. Hence, when producing rubbers for use at low temperatures, the addition of a large amount of filler is undesirable. Thus, to solve the question

* Impact strength characterizes the ability of a material to withstand rapidly applied loads.

of filler dosage the conditions of use of the finished article should be taken into account.

Considerable structural changes occur in a polymer only when the solid particles added interact with it sufficiently strongly. Good wetting of the filler by polymer is a necessary condition. A solid finely dispersed filler often plays the part of an adsorbent, taking up polymer molecules on its surface. This results in highly oriented adsorption layers which promote increased mechanical strength in the polymeric material. In a number of cases interaction between polymer and filler results in chemical compounds. Filler particle size should be in a certain correspondence with the size of the structural formations in the polymer.

Fillers are also used in plastics production. Combinations of polymeric substances with solid fillers in the form of fine high-strength fibres are called *reinforced plastics* or *reinforced polymers*. The production of reinforced polymers is necessary because the high elasticity moduli needed for structural materials cannot be obtained on the basis of polymeric substances alone. For this reason the polymers are combined with inorganic materials, primarily with silicate fibre. The fibre is the *reinforcing* material, and the polymer is the so-called *binder*, which links the fibres. Binders are usually low-viscosity oligomers which polymerize or condense (in the cold or when heated) into network polymeric compounds with a sufficiently high elasticity modulus and comparatively small elongation. The polymer serves for transferring the stress from fibre to fibre.

Reinforced systems make it possible to combine the very high strength characteristics of silicates with the elastic properties of the binder. The strength of reinforced plastics depends upon the arrangement of its fibres and the elasticity modulus of the binder. The strength of an unordered coil of entangled fibres is comparatively low, but it can be enhanced by arranging the fibres parallelly during processing. Very high strength is attained by using highly oriented fibres, in particular, the organic "steel-like" fibres mentioned above (p. 256).

Of great importance in the production of reinforced plastics is the interaction or adhesion between the binder and the fibre. The glass or other fibres should be ideally wetted by the binder, which is achieved by subjecting the glass to special treatment. Besides, processing of reinforced plastics and other polymeric materials brings up the problem of shrinkage. The processes of polymerization and polycondensation, which often occur during fabrication, are always accompanied by decrease in volume, since long chemical bonds are replaced by shorter ones (see p. 170). Opening of a double bond involves a decrease in volume of about 20 cm^3 per mole. The change in binder volume distorts the shape of the

article and gives rise to internal stresses, which affect its mechanical properties. To produce high-quality articles it is necessary to use binders which give as little shrinkage as possible.

Intelligent choice of fabrication method requires knowledge of the thermal characteristics of the polymeric materials being fabricated: thermal expansion coefficient, heat capacity, and thermal conductivity. The thermal linear and volume expansion coefficients of plastics exceed those of glass and are much larger than those of metals. For this reason, when producing reinforced materials and, in particular, articles made of a polymer and a metal, a change in size may deteriorate adhesion between reinforcing material and binder.

9.5.3. Effect of Crosslink Density on Polymer Strength

Crosslinking reactions (see p. 78) are very often used in practice to prevent flow. These reactions result in polymers of three-dimensional or network structure. Until recently it was thought that a network polymer is a number set of macromolecules with transverse chemical bonds between them. Crosslink density is characterized by the molecular mass of network chain, i.e., of the length of chain between two neighbouring crosslinks or network junctions, or by the number of moles of chain lengths between network junctions per unit volume. These quantities are related by the following equation:

$$N = \frac{\nu}{V} = \frac{\rho}{M_{\text{n. ch.}}} \tag{9.14}$$

where N = crosslink density
ν = number of moles
V = sample volume
ρ = polymer density
$M_{\text{n. ch.}}$ = molecular mass of network chain.

At present views on the structure of network polymers are being critically reviewed. Such polymers are more difficult to investigate by electron microscopy than linear polymers, but information is already available to the effect that chemical crosslinks form not only between macromolecules, but between supermolecular structures as well. Therefore $M_{\text{n. ch.}}$ is a purely equivalent quantity, which, however, gives a qualitative idea of the crosslink density: the lower the value of $M_{\text{n. ch.}}$ and the greater the ν/V ratio, the higher the crosslink density.

Crosslink density affects all the mechanical properties of polymers. For example, usually (in amorphous polymers, at any rate) elastic properties grow worse with increasing crosslink density. The glass-transition temperature rises and polymers with limiting

high crosslink densities (ebonite, rubber, etc.) are in the glassy state at room temperature. The change in strength of amorphous polymers with crosslink density is described by a curve with a maximum (Fig. 9.18). This is shown for natural rubber vulcanizates, a number of noncrystallizable synthetic rubbers, filled rubbers, and polyurethanes. The extremal nature of the strength vs. crosslink density dependence is related to the fact that the latter determines the character of the orientation and crystallization processes occurring upon deformation of the polymer.

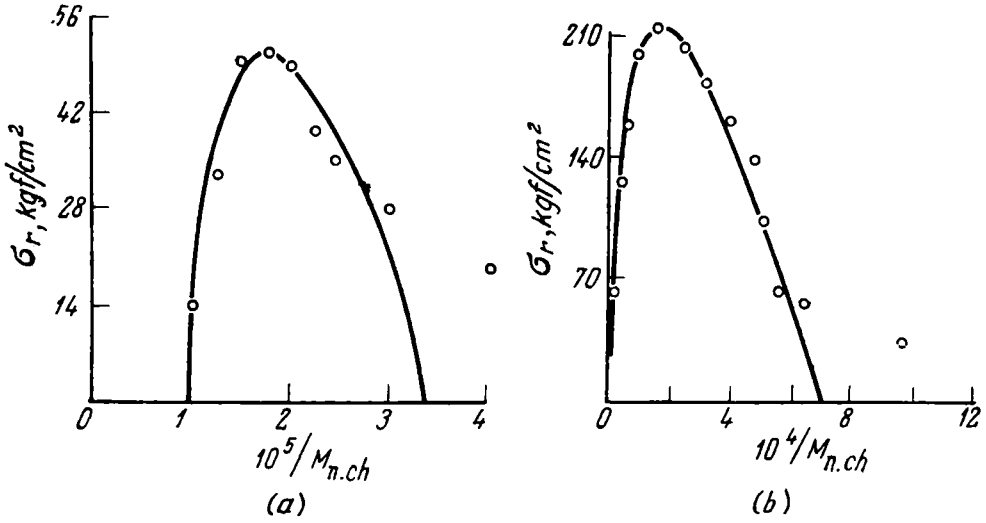


Fig. 9.18. Dependence of strength on crosslink density:
a — synthetic rubber; *b* — natural rubber

The presence of a small number of crosslinks does not hinder chain straightening during deformation, but eliminates flow processes. Therefore, the relative content of oriented or crystallized matter should increase with deformation, enhancing the crosslink density and hence the strength. After the crosslink density has become fairly high, it begins to chamber the orientation processes: the higher the crosslink density, the smaller the possibility of orientation, and the lower the strength. This explanation of the extremal nature of this dependence is confirmed by X-ray diffraction data of samples of different polymers: a maximum appears on the crystalline phase content vs. duration of vulcanization curve, which coincides with the maximum on the strength vs. crosslink density curves of the same material. The extremal nature of the strength vs. density dependence also follows from a theoretical examination of the problem.

The position of the maximum on the abscissa axis and its height (maximum strength of material) depend on the nature of the polymer, on its ability to crystallization, and on the melting temperature of the corresponding linear polymer. The more the polymer

is inclined to crystallization, and the higher its melting point, the higher will be the maximum and the more will it be shifted towards low crosslink density. In the limiting case of a polymer which crystallizes easily and is in the crystalline state at room temperature, maximum strength is observed in the linear polymer sample. Increasing the crosslink density lowers the strength monotonically, as can be seen distinctly on the example of gutta-percha.

Control of Structure Formation During Processing. Since the mechanical properties of polymers largely depend on their structure, it is attractive to create a structure ensuring an optimal set of mechanical properties which do not vary with time. The structure of a polymer is established during processing. Processing is not only imparting of a certain shape to the material, but also the creation of its structure.

Structures are often "conceived" in the melts or solutions from which the polymers are fabricated.

The higher the temperature of the melt and the longer it is held at that temperature, the less crystallization nuclei will form in it and the larger will be the spherulites produced after it is cooled. Hence, the simplest method of controlling structure is by varying the melt temperature and the rates of cooling and heating. In this way the desired structure can be "frozen", as it were.

An interesting method of structure control is by introducing artificial nuclei into the polymer melt, which then become crystallization centres. These nuclei may be various organic substances, insoluble in the polymer, melting at higher temperatures than the polymer and not interacting with it chemically (for example, indigo, alizarin). In this way a variety of supermolecular structures of the same polymer can be obtained, since they depend on the shape of the crystallites incorporated. Thus, the addition of 1% of finely dispersed indigo to a polypropylene melt during extrusion results in films of uniform small-spherulite structure. Films produced under the same conditions in the absence of artificial nuclei consist of large spherulites with distinct interfaces. The former possess forced elasticity; the latter undergo brittle fracture. Similar data have been obtained for isotactic polystyrene and gutta-percha.

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CHAPTER 10

Rheological Properties of Polymers in a Fluid State*

The mechanical properties of fluid systems are studied in the field of mechanics known as *rheology* (from the Greek words "rheos", meaning "flow", and "logos", meaning "science"). Rheological properties characterize the behaviour of polymeric systems in deformation. They determine the relationships between stress, deformation and the deformation rate. These relationships, obtained at various temperatures and under different regimes of deformation, give valuable information on the properties, structure and structural transitions of polymers of various molecular masses and polymeric systems of diverse compositions; they are very important in the consideration of problems concerning the processing of such systems.

Above the glass-transition temperature, amorphous noncured polymers are in a rubbery or a fluid state (p. 174). Crystalline polymers also pass into a fluid state above their melting point. There is no clearly-defined boundary between the rubbery and fluid states of high-molecular compounds. For polymers which exhibit both of these states, at high temperatures and low deformation rates, the determining factor is their fluidity, i.e., the ability of macromolecules to undergo irreversible directed shifts relative to one another without disturbing the integrity (continuity) of a body. Irrecoverable deformations are known also as plastic deformations. For polymeric systems in a fluid state, irrecoverable deformations may be infinitely large. If the energy needed for the irreversible displacement of macromolecules is considerably less than that of chemical bonds, the flow process is not accompanied by their breakdown.

* This chapter was written by Prof. G. V. Vinogradov.

But a polymer may become degraded at high stresses owing to the breakdown of chemical bonds, and this causes a decrease in the average molecular mass and a change in molecular-mass distribution (MMD).

10.1. PARAMETERS CHARACTERIZING THE REGIMES OF SHEAR DEFORMATION

Three simplest types of deformation are of fundamental importance in the study of the rheological properties of polymers: simple shear, uniaxial extension and triaxial compression. As regards polymers in a fluid state, their behaviour in the case of shear has been studied best of all. Let us consider the main concepts which are connected with this type of deformation, taking into account that the volume of a body being deformed does not change.

Suppose that in a polymer there are two parallel planes which are displaced relative to one another without a change in the distance between them. In this case, macromolecules, which are at different distances from the given planes, are displaced relative to one another. This displacement is the greater, the larger is the distance between them. The measure of shear deformation γ is the tangent of the angle of rotation of a straight line, which was used to determine the interplanar distance prior to deformation. Deformation is a dimensionless quantity. The deformation rate $d\gamma/dt \equiv \dot{\gamma}$ determines the change in deformation with time; it has the dimension of s^{-1}. The shear deformation rate is equal to the linear rate gradient, i.e., to a drop in the rate as a transition is made from one layer to another in the direction of its most intensive change (p. 182).

A polymer resists deformation owing to the presence of intermolecular interaction and to a change in macromolecular conformation. All the forces acting in this case on unit volume which is mentally isolated in a polymer may be reduced to a system of forces in a way shown in Fig. 10.1. If plane A moves in the direction indicated by an arrow relative to plane B, shear or tangential stresses originate on the faces of a unit cube, and they cause its skewing. In polymers which exhibit high elasticity, i.e., great reversible deformations, normal stresses perpendicular to the faces of a unit cube originate apart from shear stresses in the case of shear. The coordinate axes are marked by figures: for denoting stresses, use is made of subscripts consisting of two digits, the first of which indicates the cube face * on which stress acts, and the second one, the direction in which stresses act. The dimension of stresses is newton $\times$ m^{-2} ($Nm^{-2} = 10$ dyne$\cdot$cm^{-2}). Shear stress

* The plane is usually denoted by the direction of the normal to it.

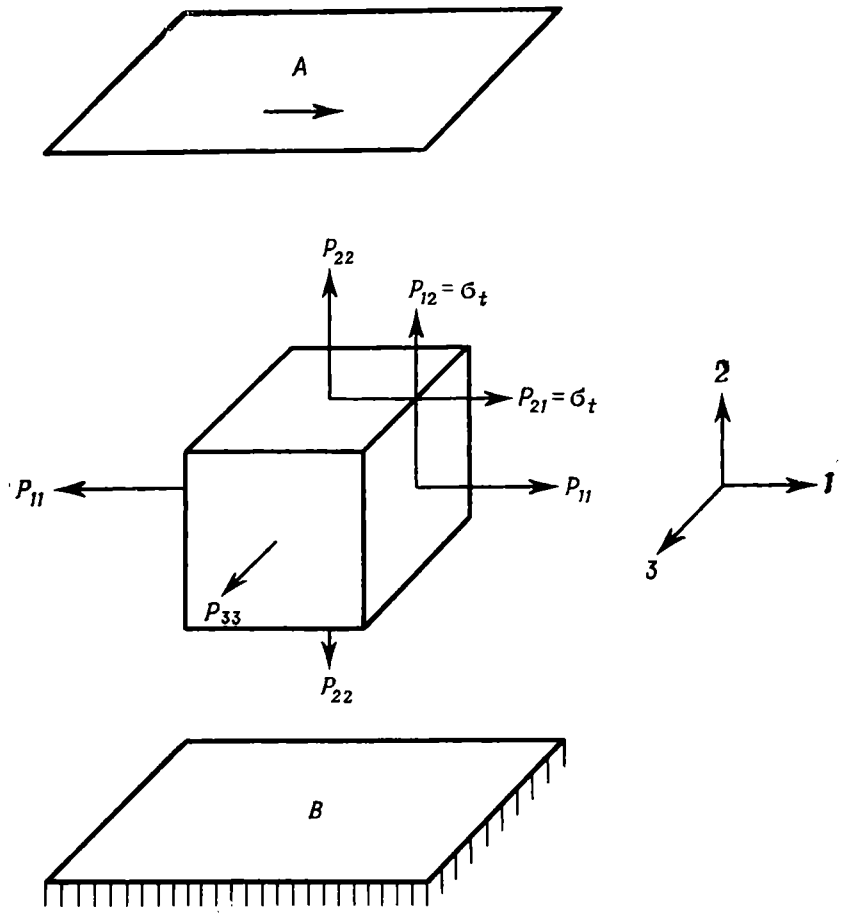

Fig. 10.1. Forces acting during shear on an element of volume of a liquid

is denoted by $P_{21} = P_{12} = \sigma_t$, while normal stresses, which compress or extend the unit cube, by P_{11}, P_{22} and P_{33}. The quantity $\sigma_w = P_{11} - P_{22}$, known as the primary difference of normal stresses, is determined most simply by experiment. Normal stresses are the reaction of polymers to the forced change in macromolecular conformations in the case of shear. They are conditioned by the tendency of molecules to assume a conformation which is the most probable one statistically.

10.2. SIMPLEST CASES OF POLYMER DEFORMATION. DEVELOPMENT OF STATIONARY FLOW

In a fluid state, many polymeric systems are viscoelastic bodies (p. 183). In them, irrecoverable and recoverable deformations develop simultaneously under the action of stress. This is accompanied with a forced change in the conformations of macromolecules and contacts between them, i.e., with a change in the structure of a polymeric system. If stresses are small, the structural changes

caused by them are compensated by the restoration of the structure under the action of thermal motion. Under these conditions, it may be assumed that the structure of a polymeric system corresponds to its initial, undeformed state.

Highly elastic (recoverable) deformation γ_e always develops more rapidly than irrecoverable flow deformation γ_r. This is illustrated in Fig. 10.2, which shows the dependencies of γ_e and γ_r on

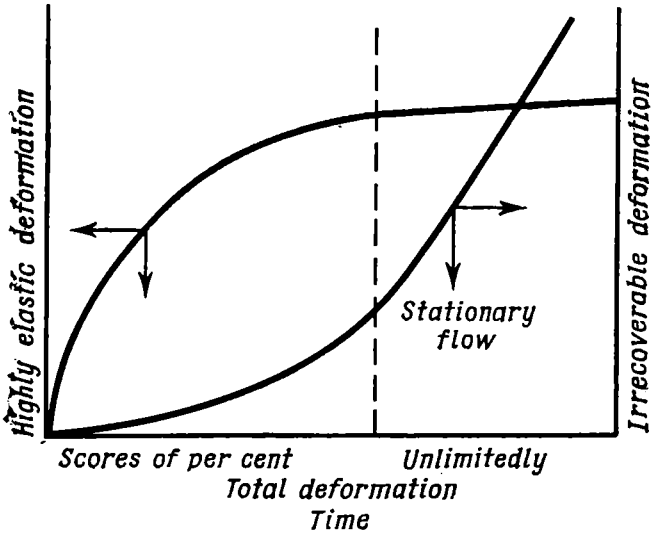

Fig. 10.2. Development of highly elastic (recoverable) and irrecoverable deformations in polymers in a fluid state at low deformation rates

total deformation $\gamma_{tot} = \gamma_e + \gamma_f$. The state of a system at which highly elastic deformation attains a constant value, while irrecoverable flow deformation increases uniformly in time, is known as the *stationary flow state*. The dynamic equilibrium of the processes of the change in structure under the action of deformation and its restoration under the action of thermal motion, and the values of rheological parameters characterizing the deformation process that are constant in time, correspond to the stationary flow state.

The most profound structural changes of a polymeric system occur in time as stresses and deformation rates increase; these changes no longer consist only in the change in the conformation state of macromolecules. The structure of a polymeric system is more or less intensively destroyed. This destruction is determined by a decrease in the number of nodes, or crosslink points, i.e., contacts between macromolecules, which form a spatial network that holds back the development of deformations. Such intermolecular interactions and spatial entanglements of macromolecules are overcome at definite critical values of stresses; this corresponds to transition through ultimate structural strength.

The destruction of crosslink points which hold back the deformation of a polymeric system causes a rapid decrease in resistance to deformation, i.e., the dissipation of stresses or *structural relaxation*, which is completed in stationary flow.

As strain increases, highly elastic deformation and stresses grow more rapidly until a structure begins to break. The ultimate critical values of highly elastic deformation and stresses grow accordingly until a structure begins to break out, i.e., ultimate strength increases. This causes the structure to break out more intensively, i.e., structural relaxation increases and stresses decrease (at a given deformation rate), or deformation rates (at a given shear stress) which correspond to stationary flow grow.

For polymolecular fluid polymeric systems, unlike solids, the transition through ultimate strength may not be accompanied by a rupture in continuity, i.e., by losses of the integrity of a body. In such systems, high-molecular components are mainly responsible for the transition through ultimate structural strength, while low-molecular fractions facilitate the rapid relaxation of stresses, i.e., the healing of microruptures, and this precludes the loss of integrity by the body being deformed. However, high stresses and deformation rates at which polymeric specimens are ruptured may be attained. Rupture characteristics (the values of γ_e, σ_t and γ_{tot} that correspond to rupture) depend on the stresses and deformation rates that are set beforehand.

High-molecular polymers of a narrow MMD are characterized by a more homogeneous structure. Therefore, the processes of their deformation are effected according to a simpler scheme: either this occurs with them as shown in Fig. 10.2, or specimens are ruptured on the attainment of definite critical parameters of deformation.

Let us now consider the simplest cases of the transition of polymolecular polymeric systems from a state of rest to stationary flow in the case of shear deformation.

Constant Shear Stress. Figures 10.3*a* and 10.3*b* represent cases of deformation at low and high constant values of shear stress σ_t. Highly elastic deformation always develops more intensively at the initial stages of deformation, but the transition to stationary flow at low and high stresses is effected differently: under the action of low stresses, total deformation grows smoothly, while at high σ_t, the γ_{tot} versus time curve becomes S-shaped and consists of three regions. The lower region corresponds to the development of mainly highly elastic deformation. Then, the growth of γ_e is retained and the breakdown of a number of intermolecular bonds begins simultaneously, and this accelerates the flow process. Such is the nature of the second S-shaped region. Constant stress acts on the decreasing with time number of bonds, and this leads to

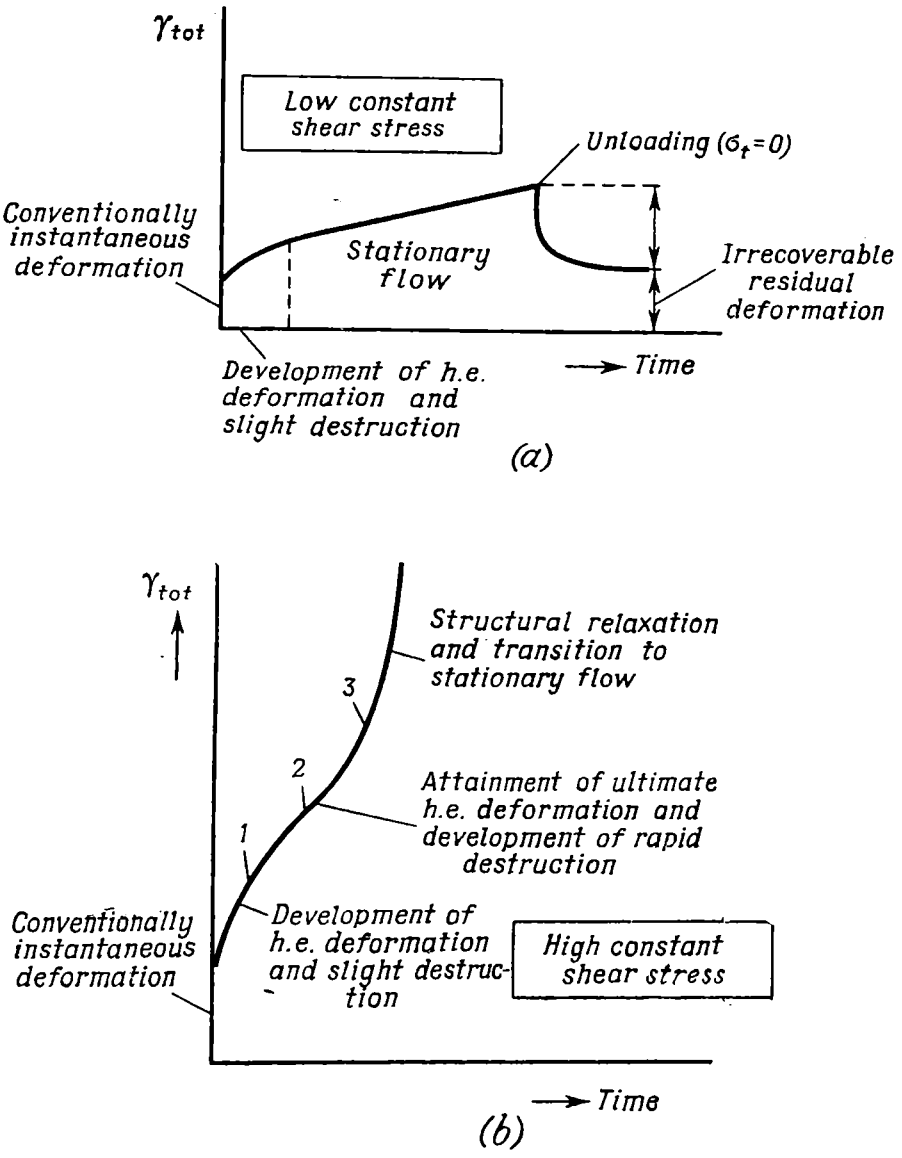

Fig. 10.3. Development of deformation with time at constant shear stresses. Elastic recoil after the removal of the load

a growth in the load on them and to the acceleration of their breakdown. This describes the transition from the second to the third steeply rising region of the curve under consideration. The length of the S-shaped region depends on the value of acting stress. When this stress is especially high, this region degenerates into a point.

Highly elastic and residual (irrecoverable) deformations are usually determined by measuring the elastic recoil of the specimen after unloading, i.e., after stress is removed (Fig. 10.3*a*).

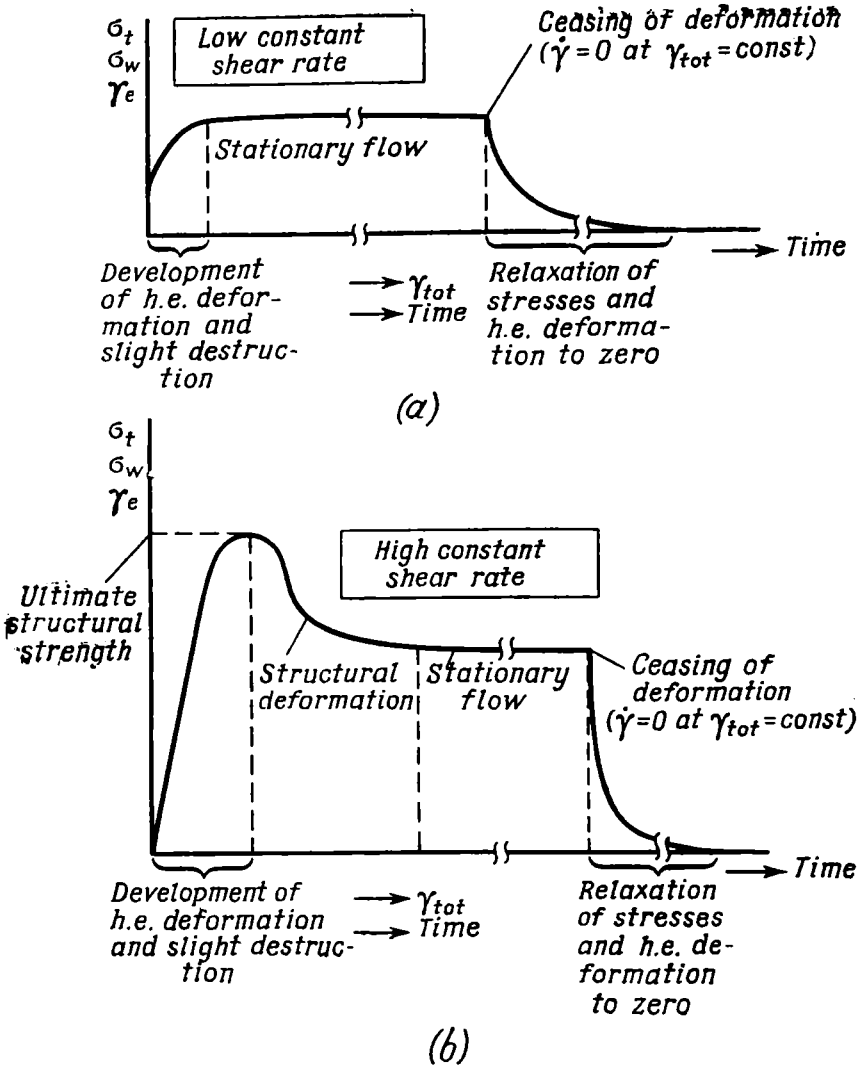

Fig. 10.4. Development of tangential stress with time at a constant deformation rate and of highly elastic deformation

The concept of conditionally instantaneous deformation or conditionally elastic deformation is sometimes used. This deformation is the part of highly elastic deformation which is registered in the course of time that is commensurable with the time during which constant stress is set. Conditional deformation, measured in the course of time close to that needed for setting certain stress, is not strictly definite and, consequently, cannot be used as a quantitative characteristic of the properties of polymeric systems.

The deformation of polymers in a fluid state at constant shear stresses is qualitatively similar to the creep of polymers in a solid or rubber-like state (Fig. 7.12). The distinction between them is that the S-shaped dependence of deformation on time for solid

polymers is observed at shear stresses which are higher than those for polymers in a fluid state by many decimal orders.

Constant Shear Rate. Figures 10.4*a* and *b* represent cases of deformation at low and high constant values of the shear rate. In both cases, σ_t, σ_w and γ_e grow on the initial regions with an increase in total deformation γ_{tot}, but the transition from the state of rest to stationary flow occurs differently. At low $\dot{\gamma}_{tot}$, the curve gradually becomes a straight line parallel to the abscissa when σ_t, σ_w and γ_e attain a constant value and $\dot{\gamma}_{fot}$ becomes equal to the irrecoverable deformation rate.

At high shear rates, a maximum appears on the curves representing $\sigma_t(\gamma_{tot})$, $\sigma_w(\gamma_{tot})$ and $\gamma_e(\gamma_{tot})$, because, up to certain critical values of σ_t, σ_w and γ_e, the development of flow and the change in the structure of a polymer do not have time to follow the growth of γ_e and γ_{tot}. When these values are attained, the polymer structure begins to change rapidly, and intermolecular bonds break causing a decrease in the resistance of a system to deformation (structural relaxation). The maximum value, σ_t^{max}, characterizes ultimate strength of a polymer, i.e., its ultimate resistance to deformation with a set rate; γ_e^{max} corresponds to the ultimate value of highly elastic deformation, which may be exhibited in a system at a set value of $\dot{\gamma}$. For polymeric systems in a fluid state, highly elastic deformations may constitute many hundreds and even thousands of per cent. After the maximum value is attained, highly elastic deformations decrease owing to the destruction of the spatial network under the action of high stresses.

Since the maximum values of σ_t, σ_w and γ_e depend on the deformation rate, they are a characteristic of the relaxation properties of a polymeric system. The process of structural relaxation is completed by a transition to stationary flow at which σ_t, σ_w and γ_e remain constant, while total deformation grows uniformly with time.

The dependencies σ_t, σ_w and γ_e on γ_{tot} are qualitatively similar. However, being obtained at the same deformation rate, they cannot be made to coincide only by changing the scales of σ_t, σ_w and γ_e.

If the deformation of a system is stopped, the constant $\dot{\gamma}_{tot}$ being fixed, stresses and γ_e are relaxed to zero, and this is a very important indication of a fluid system.

The ultimate (maximum) values of σ_t, σ_w and γ_e may be higher than the values of these quantities at stationary flow regimes by 1.5-2 times. Depending on the nature of polymeric systems, stationary flow is attained at the values of γ_{fot} which range approximately from several hundreds of per cent to 2×10^4 per cent, i.e., it may take a long time to attain this regime.

10.3. VISCOSITY

The connection between the shear rate $\dot{\gamma}$ and shear stress is expressed by Newton's law (p. 183):

$$\sigma_t = \eta\dot{\gamma} \tag{10.1a}$$

$$\log \sigma_t = \log \eta + \log \dot{\gamma} \tag{10.1b}$$

where η is the proportionality factor known as viscosity.

The dimension of viscosity is pascal $\times$ s (Pa·s). The quantity which is ten times larger is known as *poise*. Viscosity characterizes the resistance of a system to shear, or internal friction.

Depending on the nature of substances and the temperature, their viscosity in a fluid state (excluding gases and vapours) may change from 10^{-2} to 10^{13} poises. Viscosity of polymers varies from thousands (for polymers having a relatively low molecular mass) to 10^{13} poises (at glass-transition temperature).

At constant temperature and constant pressure, viscosity, i.e., the ratio of shear stress to the shear rate, may not depend on deformation conditions. The media to which this applies are known as *Newtonian media*. They include many low-molecular liquids. At ordinary shear stresses and shear rates, they do not undergo any structural change, i.e., their structure restores by thermal motion so rapidly that the external effect on this process is negligible.

At the same time, there may be cases when the effect of thermal motion on structural change, i.e., on macromolecular conformation and intermolecular contacts, is weaker than the action of shear. Depending on the relation between the shear rate and the rate of relaxation processes caused by thermal motion, viscosity, determined as the ratio $\sigma_t/\dot{\gamma}$, either may not or may depend on them. In the first case, σ_t is proportional to $\dot{\gamma}$, and in the second, shear stress changes less than the shear rate; consequently, their ratio (viscosity) decreases as shear stress and rate increase. Viscosity, which depends on σ_t and $\dot{\gamma}$, is known as *apparent* (effective) *viscosity*, and liquids whose σ_t changes disproportionately to $\dot{\gamma}$ are known as *non-Newtonian fluids*.

For one-phase polymeric systems, apparent viscosity decreases with an increase in shear stress and shear rate. This may also hold good for two-phase and multi-phase systems (latexes, suspensions). For some two-phase highly concentrated systems, an increase in the shear rate may cause a growth of viscosity. This phenomenon is known as *dilatancy*. It is observed when flow causes an increase in the number of contacts between particles of the inner phase, a process which is similar to structure formation, and, as a result, it leads to a growth in viscosity.

10.3.1. Dependence of Viscosity on the Shear Rate and Shear Stress

The simplest and at the same time the most important case of shear deformation is stationary flow, when shear rates and stresses remain invariable in time at all parts of a polymer. Under

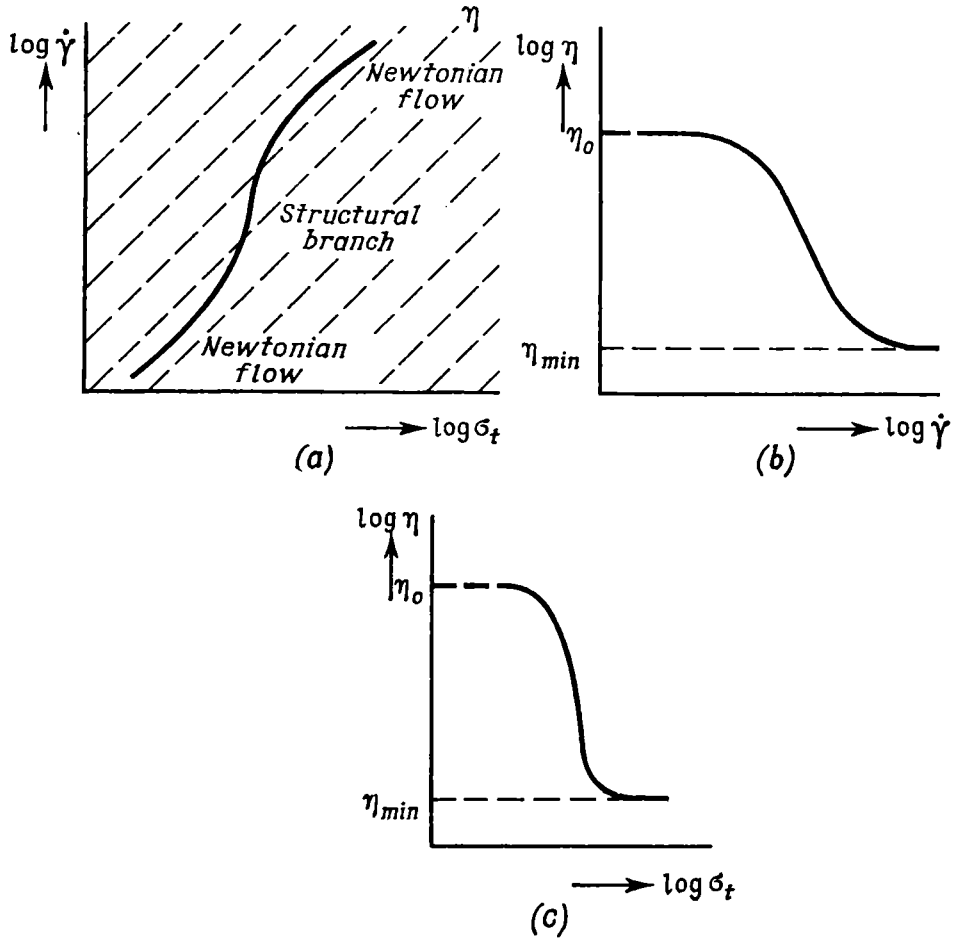

Fig. 10.5. Various methods of presenting graphically the viscous properties of non-Newtonian fluids

these conditions, highly elastic deformation is constant, and irrecoverable deformation grows uniformly in time.

Shear rates and stresses may change in a very wide range of values. Modern experimental techniques make it possible to easily change the shear rate by 10^5-10^8 times.

Equation 10.1 may be represented by curves in logarithmic coordinates in various ways (Fig. 10.5). Let us consider at first Fig. 10.5*a*. If the scales of the values of $\log \dot{\gamma}$ and $\log \sigma_t$ are the

same, the plots of the constant values of viscosity, in conformity with Eq. (10.1b), are straight lines (they are represented by dashed lines in the figure) and form angles of 45° with the coordinate axes (the slope is equal to unity).

A plot of the shear rate versus shear stress is known as the *flow curve*. It describes the totality of the stationary flow regimes having different shear rates and stresses. A typical flow curve of *non-Newtonian* fluid is shown in Fig. 10.5*a*, where it is S-shaped. At sufficiently low and high values of rates and stresses, these quantities change in direct proportion, and this corresponds to *maximum* (initial) and *minimum* Newtonian viscosities (η_0 and η_{min}); in addition, the indicated constants of viscosities meet the condition $\eta_0 > \eta_{min}$. Depending on the nature of a polymeric system and the temperature, the ratio η_0/η_{min} may change from values close to unity to several decimal orders.

Strictly speaking, initial viscosity corresponds to ultimately small shear stress, and this conforms to viscosity extrapolated to $\sigma_t = 0$, when the structure of polymeric systems corresponds to the initial state that is unchanged by deformation. But it often happens that viscosity retains the highest, initial value in a rather wide range of low values of shear rates. Then, proceeding from the measurement of viscosity, it is assumed that the rearrangement of the structure in a polymeric system under the action of shear is compensated by the effect of thermal motion, which restores the initial structure. For brevity, it is sometimes said that structural changes "do not occur" under such flow regimes. In fact, they may occur, but they are not registered when viscosity is being measured.

On the other hand, the values of σ_t and $\dot{\gamma}$ are sometimes attained at which the external effect on the structure of a polymeric system is much greater than the effect of thermal motion, and the structure does not change as shear rates and stresses increase further. This corresponds to flow regimes with constant minimum Newtonian viscosity.

The central, curvilinear region of the flow curve of non-Newtonian fluid is known as the structural branch, because, when a transition is being made from some values of σ_t and $\dot{\gamma}$ to others, a polymer changes its structure under the action of shear in this range of their values, and this is easily detected by measuring viscosity. The change is expressed in the dependence of the ratio $\sigma_t/\dot{\gamma}$ on shear stresses and rates, i.e., in the disproportion of the values of σ_t and $\dot{\gamma}$. Each point on the structural branch of the flow curve corresponds to a state of dynamic equilibrium between the processes of a change and restoration of a structure. An increase in the intensity of deformation causes a shift in equilibrium towards a greater structural change in comparison with the states

at which $\eta = \eta_0$. A decrease in this intensity or the cessation of deformation causes the restoration of a structure which was at rest. Consequently, the states and structure of polymeric systems reversibly change in flow. This phenomenon always occurs in time and is known as *thixotropy*. The kinetics of establishing equilibrium states in the case of deformation and rest is important to the characteristics of thixotropy, and this kinetics is determined by the regime of deformation, the temperature and the nature of a polymeric system. It sometimes takes a long time to attain the state of dynamic equilibrium and the complete recovery of the structure of a system at rest.

Besides flow curves, use is often made of viscosity versus rate curves, which show how the ratio $\sigma_t/\dot{\gamma}$ changes depending on the shear rate. The typical viscosity-rate curve of the non-Newtonian fluid is shown in Fig. 10.5*b*.

In the not very wide range of change in variables, the connection between shear stress and shear rate, and the dependence of viscosity on the shear rate are described by simple empirical formulas:

$$\dot{\gamma} = k\sigma_t^{\nu} \tag{10.2a}$$

$$\eta = \frac{1}{k}\dot{\gamma}^{-(1-1/\nu)} \tag{10.2b}$$

where $\nu > 1$.

There may also be a third type of plots, which describe the regimes of stationary flow of non-Newtonian media, when the dependence of η on σ_t is considered (see Fig. 10.5*c*). Curves which correspond to this dependence are characterized by greater steepness in comparison with viscosity-rate ones. Curves represented in Fig. 10.5*a*, *b* and *c* equally describe the properties of polymeric systems.

Curves consisting of three regions characterizing the stationary flow of non-Newtonian media are known as complete curves. They are obtained in the study of the following types of polymeric systems:

(1) polymers of low molecular mass;
(2) dilute polymer solutions;
(3) concentrated polymer solutions in which macromolecules do not exhibit high kinetic flexibility.

The lower part of the flow curve, close to the region of initial Newtonian viscosity, is registered most reliably. At the same time, the initial Newtonian viscosity of polymeric systems, which exhibit a strong dependence of effective viscosity on the shear rate, may correspond to very low values of the rate, and this hinders direct measurements of η_0. This is especially typical of high-molecular polymers of wide molecular-mass distribution.

In such cases, in order to determine the value of η_0, it is necessary to extrapolate viscosity to the zero value of shear stress, and this is done graphically in the coordinates log η versus σ_t.

There are some difficulties in measuring viscosity at high shear rates and stresses. One of them is due to the fact that macromolecules do not have time to move in space relative to one another under these conditions of deformation. They retain the ability to only undergo rapid conformation changes. Under such conditions, a linear polymer passes into a forced rubber-like state, i.e., it behaves as a quasicured system, whose deformability is limited. As a result, at high stresses, continuity is ruptured and flow is replaced by the slipping of a polymer relative to the solid wall with which it is in contact. Laminar flow and the adhesion of a polymeric system to the wall relative to which it moves are thus disturbed, i.e., the main conditions for measuring viscosity are violated.

Fig. 10.6. Distortion of a cylindrical stereoregular rubber extrudate at high shear stresses

The origination of ruptures in a polymeric system or its detachment from walls makes it possible for relaxation processes to occur in these regions and, consequently, for ruptures to "heal". These opposite by their nature phenomena, which occur successively and continuously, impart a vibrational character to the entire process. Such a character of polymer flow at elevated shear stresses and rates distorts extrudates coming out of caps. This is illustrated by a photograph of a stereoregular rubber extrudate from a cylindrical capillary tube (Fig. 10.6).

At even higher rates, ruptures in a polymer become so intensive that, at a given pressure drop in a duct, its resistance to motion sharply decreases and the volume output may increase by tens, hundreds and even thousands of times. The phenomenon of a sharp decrease in resistance and a jumpwise increase in the rate of motion of a polymer under the action of its ruptures is known as flow spurt or simply *spurt*.

Another difficulty is heat generation in liquid flow as a result of internal friction, which disturbs the isothermal nature of flow. Indeed, the work of the forces of viscous friction per unit volume of a liquid is equal to the product of shear deformation by shear

stress, i.e., $\gamma\sigma_t$. The intensity of heat generation is determined by friction power (by the work of friction forces per unit time), and it is equal to $\dot{\gamma}\sigma_t$. Proceeding from Eq. (10.1), the expression $\eta\dot{\gamma}^2$ is obtained for the internal friction power. It follows that in the case of internal friction, heat generation in polymers increases very rapidly with a growth of the shear rate and viscosity, which in turn increases with a growth in molecular mass.

10.4. SPECIFIC FEATURES OF THE POLYMER FLOW OF NARROW AND WIDE MOLECULAR-MASS DISTRIBUTION

Polymers having narrow molecular-mass distribution (MMD) are now available owing to successes made in anionic polymerization (p. 52) and fractionation (p. 365). A study of the rheological behaviour of such linear polymers of high molecular masses has made it possible to ascertain several fundamentally new regularities and, in particular, understand the causes of the deviation of viscous properties of polymeric systems from Newton's law.

Linear polymers with $M \gg M_{crit}$ (p. 284) and narrow MMD, when they are considerably away from the glass-transition temperature, digress inconsiderably from Newtonian behaviour in a very wide range of shear stresses, even up to critical shear rates ($\dot{\gamma}_c$) which conform to the transition of polymers to a forced rubber-like state.

Critical shear rates are inversely proportional to initial viscosity. Then, according to Newton's law, their product determines the critical values of shear stress σ_{tc}. This quantity is constant within the limits of every polymer homologous series, and it practically does not depend on temperature. For various polymer homologous series, the value of σ_{tc} changes in a narrow range, approximately from 0.05 to 0.5 MNm^{-2}, while $\dot{\gamma}_c$ may change, like initial (maximum) viscosity, in the range of many tenths of orders, depending on molecular mass and temperature. The values of $\dot{\gamma}_c$ and σ_{tc} correspond to the spurt.

If two monomolecular polymers of a different molecular mass are mixed together, their mixture may exhibit non-Newtonian flow, because, as the shear rate increases, a high-molecular polymer first of all passes into a rubber-like state, while a low-molecular component still retains its ability to flow. Being in a rubber-like state, a high-molecular polymer acts as an elastic filler. The resistance to the deformation of such a system is determined by losses due to friction of a low-molecular component, which is in a fluid state, by its streamlining of macromolecules of a high molecular mass, and by losses connected with the rapid conformation transitions of both components of a mixture.

However, since losses due to friction of a high-molecular component are now absent, the losses of a polymeric system decrease on the whole. As a result, the shear rate increases more rapidly than stress, and this corresponds to a decrease in viscosity, i.e., to a deviation from Newton's law. In Fig. 10.7, the dashed line is the flow curve of a binary mixture, which is characterized by the same critical shear stress as that of its components.

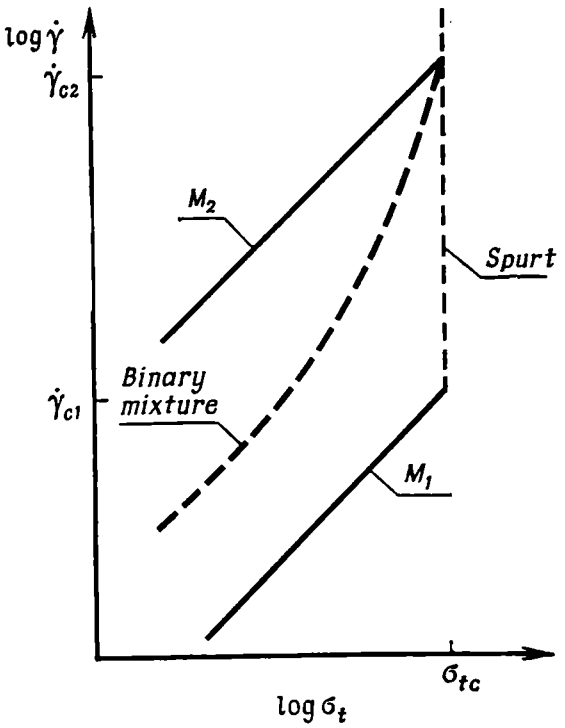

Fig. 10.7. Flow curves of polymers of narrow molecular-mass distribution and of their mixtures ($M_1 > M_2 > M_{crit}$)

For monomolecular polymers having M not much higher than M_{crit}, the structure changes more readily under the action of shear. Therefore, for low-molecular polymers having even a narrow MMD, non-Newtonian flow can be observed when shear stresses are comparatively low.

As temperature drops and approaches T_g, thermal motion becomes less intense and the restoration of a polymer structure, changed by applied shear stress, is hampered. In such cases, a deviation from Newton's law can be detected for high-molecular polymers having a narrow MMD.

The foregoing shows that non-Newtonian flow is one of the manifestations of the relaxation nature of polymeric systems, and it is all the more noticeable, the higher is the polymolecularity of a polymer. Therefore, if two polymers having the same weight-

average molecular mass $\bar{M}_w$, but different MMD, are compared, the anomaly of viscosity is more pronounced for systems having greater polydispersity.

10.5. INITIAL NEWTONIAN VISCOSITY OF POLYMERIC SYSTEMS

The most important parameter characterizing the properties of polymers in a fluid state is initial Newtonian viscosity, which depends on temperature and molecular mass.

10.5.1. Effect of Temperature on Initial Newtonian Viscosity

The possibility of the displacement of molecules in liquids is determined by two factors: the presence of a free volume in them (p. 164) and the overcoming of forces of intermolecular interaction. These displacements may occur spontaneously under the action of the thermal motion (self-diffusion) of molecules. The directed displacement of molecules in flow requires the application of force, which supplements the action of thermal motion. The dependence of the viscosity of a liquid on free volume was first indicated by Bachinsky. A more precise experimental equation connecting viscosity with free volume was proposed by Doolittle:

$$\ln \eta_0 = a + b\frac{V_0}{V_{f,g}} \simeq a + b\frac{V_0 + V_f}{V_{f,g}} = a + b\frac{V}{V_{f,g}} \qquad (10.3)$$

where a and b = constants (b is close to unity) which characterize the nature of a liquid (polymer)
V_0 = proper volume of molecules per unit mass of a substance
V_f = its free specific volume.

Molecules of amorphous polymers can move only above their glass-transition temperature T_g; at $T = T_g$, the free volume of a gram of all polymers constitutes the same fraction of their specific volume, which is approximately 0.025 (2.5 per cent). Therefore, T_g is usually taken as the starting point in reading temperature, and the free volume at any temperature higher than T_g is calculated by the equation

$$V_f = V_{f,g} + \alpha V_{f,g}(T - T_g) \qquad (10.4)$$

where V_f and $V_{f,g}$ = specific free volume of a polymer at T and T_g, respectively
α = thermal coefficient of expansion at $T > T_g$.

If Eq. (10.3) is written for two temperatures and Eq. (10.4) is substituted in it, we obtain the Williams-Landel-Ferry equation (p. 201):

$$\ln \frac{\eta_g}{\eta} = \frac{bV}{V_{f,g}} \cdot \frac{T - T_g}{V_f/\alpha \cdot V_g + (T - T_g)} = \frac{40\,(T - T_g)}{50 + (T - T_g)} \qquad (10.5)$$

where η and η_g = viscosity at T and T_g, respectively.

This equation is well justified in the temperature range $T_g < T < (T_g + 120)$. Since it may be taken that $\eta_g = 10^{13}$, the dependence of viscosity on temperature in the given range of its values is determined only by the remoteness of the given temperature from T_g.

At temperatures at which free volume becomes sufficiently large, the dependence of the viscosity of a liquid (polymer) on temperature is decisively affected by the overcoming of the forces of macromolecular interaction, and this enables the segments of macromolecules to jump over from one equilibrium position to another. This process is connected with the overcoming of the potential barrier in the same way as in the transformations of molecules in chemical reactions. The height of this barrier is characterized by the free energy of activation of viscous flow ΔG_{visc}.

The Frenkel-Eyring activation theory yields the following expression for the temperature dependence of viscosity:

$$\eta_0 = Ae^{\frac{\Delta G_{visc}}{RT}} = \frac{N_A h}{V} \cdot e^{\frac{\Delta G_{visc}}{RT}} \qquad (10.6)$$

where V = molar volume
T = absolute temperature
R = universal gas constant
N_A = Avogadro number
h = Planck constant.

If it is taken that $\Delta G_{visc} = \Delta H_{visc} - T\Delta S_{visc}$, Eq. (10.6) will assume the form

$$\eta_0 = \frac{N_A h}{V} \cdot e^{-\left(\frac{\Delta S_{visc}}{R}\right)} \cdot e^{\left(\frac{\Delta H_{visc}}{RT}\right)} \qquad (10.7)$$

where ΔH_{visc} = heat of activation of viscous flow, i.e., the amount of heat which must be fed to one mole of particles for effecting the act of a jump in flow
ΔS_{visc} = entropy of activation of viscous flow.

After combining the terms which do not depend or slightly depend on temperature and then taking the logarithm, we obtain

$$\log \eta_0 = \log A' + \frac{\Delta H_{visc}}{2.303RT} \qquad (10.8)$$

where A' = constant.

According to Eq. (10.7), the dependence of the logarithm of viscosity on inverse temperature must be expressed by a straight line whose slope can be used to calculate the value of the heat of flow activation ΔH_{visc}.

In the case of the nonlinear dependence of $\log \eta_0 = f\left(\frac{1}{T}\right)$, the so-called apparent heat of activation of flow, which is a function of temperature itself, is calculated:

$$\Delta H_{app} = \frac{d \log \eta}{Rd\,(1/T)} \tag{10.9}$$

The determination of the values of ΔH_{visc} for polymers and their comparison with those of ΔH_{visc} for low-molecular compounds of a similar structure were particularly important in understanding the mechanism of polymer flow. It turned out that an increase in the molecular mass of low-molecular compounds causes only a restricted growth of ΔH_{visc}, whose limiting values are attained at molecular masses which are inconsiderable in comparison with those of polymers. It follows that the temperature dependence of polymer viscosity is determined by the dimensions of not macromolecules, but of their small parts — segments, which are kinetically independent structural elements of a polymer. It is the segments that shift (jump) from one position to another under the action of thermal motion. Segments usually include, at the most, 30-40 atoms of the main chain of macromolecules. Since the mechanism of polymer flow is segmental, the heat of activation relates to the mole of segments in the dimensions of the quantity ΔH.

The heats of activation of viscous flow and, accordingly, the dependence of viscosity on temperature are determined by the nature of macromolecules. The kinetic flexibility and regularity of the structure of a polymer chain, the type of branches and the presence of polar groups in a macromolecule are of great importance. As regards carbon-chain polymers, the lowest values of ΔH are possessed by stereoregular 1,4-*cis*polybutadiene ($\sim$5 kcal/mole) and linear polyethylene ($\sim$7 kcal/mole). As to polyethylene of high pressure, whose macromolecules are branched to a comparatively small extent, the value of ΔH rises to 11-12, while for polyisobutylene, it reaches approximately 15 kcal/mole. For polystyrene, whose side groups are phenyl rings, ΔH rises to 28; ΔH is even higher for polyvinyl chloride and polyvinyl acetate (35 and 60 kcal/mole, respectively).

10.5.2. Effect of the Molecular Mass on Initial Viscosity

For the entire macromolecule to move, many segments must undergo cooperated movement. This means that the resistance of a

macromolecule in duct must depend on its molecular mass. Indeed, the viscosity of a polymer sharply grows as its molecular mass increases. In recent years, the dependence of viscosity on molecular mass, common for many polymers, was shown on the basis of an investigation of flow of great number of polymers; this dependence may be represented by two intersecting straight

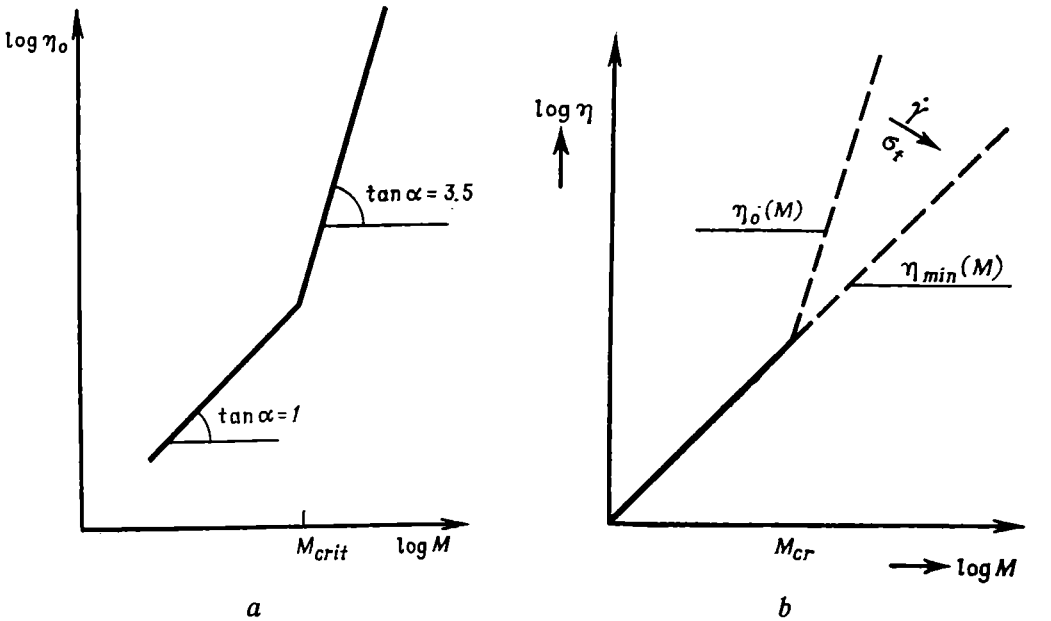

Fig. 10.8. Change in the rate of dependence of polymer viscosity on molecular mass in the region of its critical value (*a*) and effect of the shear rate and shear stress on the dependence of polymer viscosity on molecular masses which are higher than their critical values (*b*)

lines in the log-log coordinates (Fig. 10.8*a*). The value of the molecular mass that matches to the point of intersection of these straight lines became known as critical molecular mass M_{crit}, and the degree of polymerization corresponding to it, the critical degree of polymerization P_{crit}. The quantities M_{crit} and P_{crit} practically do not depend on temperature.

In the region of shear rates and stresses, where polymers behave as non-Newtonian fluids, viscosity becomes less dependent on molecular mass as the intensity of their deformation increases (Fig. 10.8*b*).

For linear polymers having flexible chains, the dependencies of initial viscosity on molecular mass were ascertained empirically:

$$\eta_0 = K_1 M^{3.5} \qquad \text{for } M > M_{crit} \tag{10.10}$$

$$\eta_0 = K_2 M \qquad \text{for } M < M_{crit} \tag{10.11}$$

In this case, the molecular masses may be taken equal to their weight-average values ($\bar{M}_w$); K_1 and K_2 are constants.

As regards linear nonpolar and weakly polar polymers, the value of M_{crit} changes in the range of a decimal order (approximately from 4000 to 40 000). The critical value of the length of macromolecules, determined by the number of atoms in the main chain, changes even to a smaller extent (approximately thrice). The values of M_{crit} are tens of times greater than the mass of kinetic segments, whose jump from one position to another causes the flow of polymeric systems (p. 101).

The connection between the constants K_1 and K_2, on the one hand, and density and parameters characterizing macromolecules (root-mean-square radius of gyration, molecular mass, microscopic coefficient of friction of groups forming a chain, etc.), on the other, was ascertained mainly in the works by Fox (p. 304).

It follows from Eqs. (10.10) and (10.11) that in the case of average molecular mass which is higher than the critical one, initial Newtonian viscosity grows very sharply with an increase in $\bar{M}_w$, because, at $M > M_{crit}$, a stable spatial fluctuational network is formed in a polymeric system as a result of contacts between macromolecules or their aggregates.

The physical nature of a fluctuational network is determined by the fact that the nodes of contact between macromolecules and their associates are continuously formed and disintegrate, and the associates themselves are also formed and disintegrate, under the action of thermal motion. The fluctuational spatial network is usually called the "entanglement network" for the sake of brevity. At rest and at constant temperature, the density of nodes of a fluctuational network on the average (in time) remains constant.

The critical value of molecular masses and its multiple values are important to the entire set of viscoelastic properties of polymers. For example, large recoverable (highly elastic) deformations appear in high-molecular compounds only at $M > M_{crit}$. Therefore, it is expedient to compare the properties of specimens in various polymer homologous series not at equal absolute values of molecular masses, but with regard to how much they are greater than M_{crit}. Viscoelastic properties of high-molecular polymers must be compared by their molecular masses reduced to M_{crit}, i.e., according to the M/M_{crit} ratio.

Since at $M > M_{crit}$ initial Newtonian viscosity depends greatly on weight average molecular mass $\bar{M}_w$, a change in $\bar{M}_w$ in high-molecular polymers is registered far more accurately when the initial Newtonian viscosity of a melt of a polymer is being measured than when its intrinsic viscosity (p. 457) is being measured.

Polymolecularity (at given $\bar{M}_w$) does not strongly affect the value of initial Newtonian viscosity. At the same $\bar{M}_w$, initial Newtonian viscosity decreases as macromolecules become more branched. When the side chains are very long (star-like and comb-like

polymers), initial viscosity depends to a far greater extent on molecular mass than described by Eq. (10.10).

Our consideration of the dependence of initial Newtonian viscosity on temperature and molecular mass shows that the effect of these two extremely important factors can be divided. Then, according to Fox and Flory, we may write

$$\eta_0 = f_1(T)\, f_2(M) \tag{10.12a}$$

$$\log \eta_0 = \log f_1(T) + \log f_2(M) \tag{10.12b}$$

10.6. APPARENT VISCOSITY

Apparent viscosity depends on shear stress, and, according to Bartenev, Eq. (10.12b) may be generalized by introducing a term which expresses the effect of this stress, i.e.,

$$\log \eta_{ap} = \log f_1(T) + \log f_2(M) + \log f_3(\sigma_t) \tag{10.13}$$

This equation is valid for bulk polymers at shear stresses which are not too high, i.e., when they are lower than stress which corresponds to the inflection point on the curves of the dependence of viscosity on shear stress (Fig. 10.5).

Apparent viscosity depends on temperature, but at high values of the parameters of deformation, i.e., when deformation is very intensive, the effect of temperature on viscosity decreases. This appears in the fact that flow curves form a converging set in the region of high shear rates and stresses (Fig. 10.9). This affects the heat of activation of viscous flow, which is calculated on the basis of such curves.

In the region of Newtonian flow, when shear stress is proportional to the shear rate, the quantity $\Delta(\log \eta)_{T_1-T_2} = \log \eta_{T_1} - \log \eta_{T_2}$ does not depend on how viscosities are compared for various temperatures at constant shear stress or at constant shear rate. Apparent viscosity depends on shear stress and rate and, consequently, its change with temperature may be estimated at constant shear stresses or at constant shear rates. These two ways of determining the effect of temperature on apparent viscosity are unequal, as can be seen from the family of flow curves of polyethylene obtained at different temperatures (Fig. 10.9). The flow curves in this figure correspond to temperatures of 130, 150, 170, 190, 210 and 230 °C. Vertical dashed lines give the section of flow curves at constant shear stresses, and horizontal ones, at constant shear rates.

In the given temperature range, the heat of activation of viscous flow is determined by the following quantity in conformity with

Eq. (10.7):

$$\Delta(\log\eta)_{T_1-T_2} = \log\eta_{T_1} - \log\eta_{T_2} = \log\left(\frac{\sigma_t}{\dot\gamma}\right)_{T_1} - \log\left(\frac{\sigma_t}{\dot\gamma}\right)_{T_2} =$$

$$= \Delta(\log\sigma_t)_{T_1-T_2} - \Delta(\log\dot\gamma)_{T_1-T_2} \quad (10.14)$$

When the shear rate at which $\Delta(\ln\eta)$ is determined increases, its value decreases, as is evident from a decrease in the length of the horizontal dashed regions in Fig. 10.9. At the same time, the

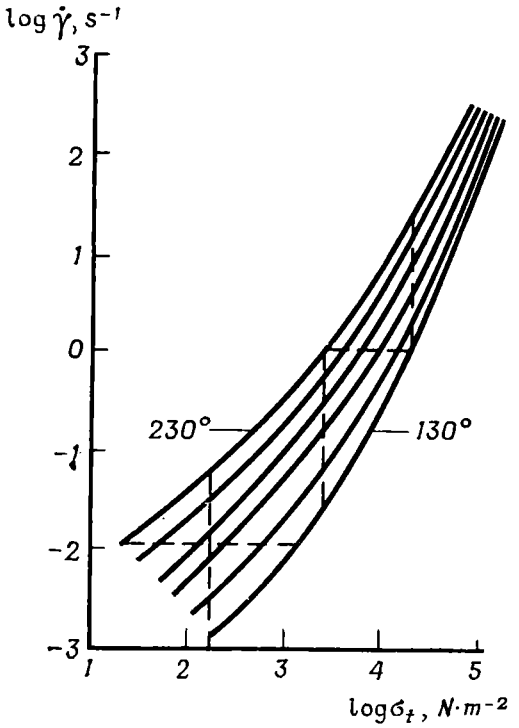

Fig. 10.9. Flow curves for high-pressure polyethylene at various temperatures

lengths of vertical dashed regions which correspond to different constant values of shear stresses undergo little change. This means that at different constant shear stresses, the straight lines of dependence of $\Delta(\log\eta)$ on $1/T$ are practically parallel, while they diverge at different constant shear rates. Consequently, it may be assumed in the first approximation that the heats of activation of viscous flow, which are determined at different constant values of shear stresses (in equally stressed states), have the same values as on regimes of flow with initial Newtonian viscosity. This is valid only at small deviations from the flow regime with initial Newtonian viscosity, when the principle of temperature-independent viscosity characteristics of polymeric systems that is considered below holds good.

Hence, the dependence of viscosity on temperature is the greatest for $\eta = \eta_0$. The heat of activation in the region of minimum Newtonian viscosity is less than that in the region of initial viscosity, and the heat of activation, like at $\eta = \eta_0$, does not depend on whether it is determined at a constant shear stress or at a constant shear rate.

10.7. TEMPERATURE-INDEPENDENT VISCOSITY CHARACTERISTICS

It is expedient to compare various states of polymeric systems at the stationary flow regime by taking, as the basic state, a state in which viscosity is initial and the flow process is described by Newton's equation, i.e., various states are compared with the state in which the structure of a polymeric system is taken as being the same as that at rest. The measure of changes in a state is the ratio of viscosity at given values of shear stress and rate to initial Newtonian viscosity. The quantity $\eta_r = \eta/\eta_0$ is known as reduced viscosity. It shows how a change in the state of polymeric systems affects viscosity in the course of flow.

A description of the viscous properties of polymeric systems in a form which does not depend on temperature is of great practical importance, since it substantially facilitates the estimation of viscosity and may make its experimental determination unnecessary. Such temperature-independent characteristics of polymeric systems are obtained when considering the dependence of reduced viscosity on a parameter that determines the intensity of deforming action on polymeric systems. The measure of this intensity may be the relationship between the deformation rate and the rate of dissipation of stresses in the system being deformed. Since the stress dissipation rate is a quantity inverse to relaxation time, the dimensionless parameter which is equal to the product of the deformation rate by relaxation time should be taken as the measure of intensity of deformation. Although polymers are characterized by the totality of relaxation times, there is an unambiguous connection between them. This makes it possible, at least in the first approximation, to consider characteristic relaxation time to be its initial value equal to η_0/G_e^0, where G_e^0 is the initial modulus of high elasticity (see below).

For a large number of industrially-produced linear bulk polymers, the values of G_e^0 are in a narrow range of values: from 10^3 to 10^4 Nm^{-2}. Moreover, G_e^0, unlike η_0, changes very little with temperature. Hence G_e^0 can be assumed constant. Consequently, the intensity of the deformation effect must be estimated by a parameter known as the reduced shear rate $\dot{\gamma}_r = \eta_0\dot{\gamma}$. Its dimension is

Nm^{-2}. Thus, the viscous characteristics of bulk polymers can be represented in a temperature-independent form as the dependence of reduced viscosity on the reduced shear rate.

To obtain the temperature-independent characteristics of polymer viscosity, it is necessary to know the dependence $\eta_0(T)$.

Since, in the method of plotting universal temperature-independent characteristics of the viscous properties of polymers, the reference state is taken as the state in which $\eta = \eta_0$, the method is valid only at small deviations from this state, at any rate, with

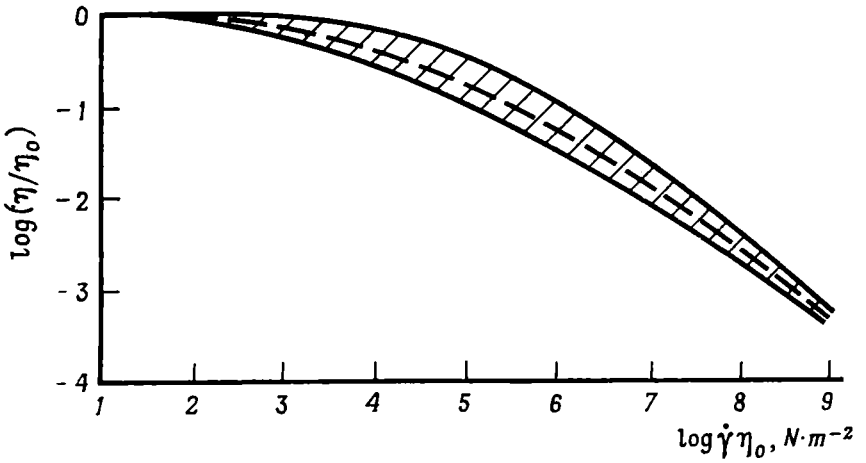

Fig. 10.10. Universal temperature-invariant viscous characteristics of polydisperse polymers. The dashed line is averaged dependence

shear stresses and rates that are not higher than those corresponding to the inflection point on flow curves.

The dependence of reduced viscosity on the reduced shear rate turns out to be not only temperature-independent, but also, up to a certain approximation, universal for many industrially-produced linear polymers, i.e., the results of measurements of the viscosity of polymers of a diverse nature at different temperatures are the same. Since the universality and temperature invariance of the dependence of polymer viscosity on temperature and on the shear rate are valid only up to a certain approximation, it is represented graphically as a band in the coordinates $\log \eta_r$ vs. $\log \dot{\gamma}_r$ (Fig. 10.10). Temperature invariance and the universality of the dependence of η_r on $\dot{\gamma}_r$ are not satisfied when the dependencies of viscosity on temperature for polymers of wide and narrow molecular-mass distributions are being compared.

10.8. HIGH ELASTICITY OF POLYMERIC SYSTEMS

An extremely important feature of polymeric systems is their ability to undergo rubber-like, or highly elastic, i.e., great, recoverable deformations (γ_e), and this is connected with the presence

of a continuous spatial entanglement network formed by flexible macromolecules and their associates.

Liquids which exhibit rubber-like properties are known as elastic ones. Under the action of deformation, they exhibit many remarkable features, which are known by the common term of Weissenberg effect. For example, when a rod revolves in an elastic liquid, the liquid "winds" itself on the rod and may rise along it to a considerable height. Ordinary Newtonian liquids under the same conditions are thrown away from the revolving rod under the action of the centrifugal force. If a hollow cylinder is revolved in an elastic liquid, the liquid rises inside the cylinder. Elastic liquid which fills the gap between two parallel discs, one of which is put into rotation, tends to draw them apart, and pressure develops along the axis of the discs.

Elastic liquid may be put in an annular clearance between coaxial cylinders. Suppose that the inner light cylinder is suspended on an elastic torsion bar, while the outer cylinder rotates. The torque is then transmitted through elastic liquid to the twisted inner cylinder. When the outer cylinder stops, the inner cylinder begins to rotate in the opposite direction under the action of the elastic recovery of liquid. By the value of this rotation, i.e., elastic recoil, the value of highly elastic deformation is determined.

The connection between recoverable deformation and shear stress for solids is determined by Hooke's law: $\sigma_t = G\gamma$, where G is the modulus of elasticity (p. 179). This law may be generalized for highly elastic deformations. Then,

$$\sigma_t = G_e\gamma_e = \frac{1}{J_e}\gamma$$

where G_e and J_e are the modulus and the coefficient of compliance of highly elastic deformations in shear, respectively. Hooke's law for highly elastic deformations is strictly valid for σ_t which tends to zero. These conditions are met by $G_e = G_e^0$ and $J_e = J_e^0$, where G_e^0 and J_e^0 are the initial (minimum and maximum, accordingly) values of the modulus and coefficient of compliance. The quantities G_e^0 and J_e^0 often turn out to be practically constant in the finite range of the change in σ_t.

The elasticity modulus has the dimension of Nm^{-2}. When shear stress and rate increase, γ_e grows, but slower than stress, and, consequently, the ratio σ_t/γ_e grows as stress increases. In this case, the shear modulus may increase by tens of times. Modulus of high elasticity, which depends on shear stress, is known as the *apparent modulus.*

An increase in G_e (or a decrease in the compliance coefficient) of a polymeric system with a growth in shear stress is caused by

a change in the conformation of macromolecules in the course of deformation: they uncoil and straighten out. As stress grows, the number of possible conformation states diminishes, and this is equivalent to an increase in the rigidity of macromolecules and the whole spatial network.

When polymeric systems at flow regimes have high elasticity, it means that there is a continuous spatial structure (network) in their duct. Stationary flow regimes correspond to the quasi-equilibrium values of highly elastic deformation. These quasi-equilibrium deformations have such a name to distinguish them from equilibrium values which correspond to static equilibrium, while, in stationary flow, equilibrium is dynamic.

The quantities G_e and J_e depend to a very small extent on temperature.

Measurements of highly elastic deformations of linear polymers of narrow MMD have shown that great recoverable deformations are exhibited at $M \geqslant M_{crit}$, when a continuous spatial network is formed in polymers. Under these conditions, the density of the nodes of the network is low and is characterized by high compliance to which very low values of G_e^0 correspond. When the value of M increases to $M = (2 \text{ to } 3)\, M_{crit}$, the value of G_e^0 grows to 10^4-10^5 Nm^{-2}. When the values of M are even higher, the initial values of shear moduli and compliance coefficients no longer depend on molecular mass. Another peculiarity of high-molecular polymers of narrow MMD is that recoverable deformations at flow regimes as a rule do not exceed 200-250 per cent. This characterizes them as rigid polymeric systems. At shear rates and stresses which correspond to the indicated values of γ_e, high polymers pass over from a fluid state to a forced rubber-like state in which fluidity is suppressed, and deformability is limited. Therefore, the continuous deformation of polymers which are in a rubber-like state causes the rupture of specimens. In this case, the higher the stress, the greater is the value of γ_e, but the less is the time taken from the beginning of deformation to the rupture of specimens.

Polydispersity greatly affects the high elasticity of polymeric systems. The shear moduli of polymer mixtures are usually lower, while compliance is higher, than those of separate components. Relatively inconsiderable concentrations of high-molecular polymers especially strongly affect the growth of compliance. Recoverable deformations in polydisperse polymeric systems in a fluid state may reach 1000 per cent and even more.

As regards polymers which exhibit high elasticity, shear deformation sometimes causes very considerable normal stresses, which produce the Weissenberg effect. The simplest method of determining the primary difference of normal stresses is based on the mea-

surement of the axial force which tends to draw apart two parallel planes that rotate relative to one another and between which a polymer is situated. This makes it possible to find empirically

$$\sigma_w = P_{11} - P_{22}$$

According to Lodge, σ_t is simply connected with the modulus of high elasticity in shear G_e and highly elastic shear deformation γ_e, which correspond to the given value of shear stress:

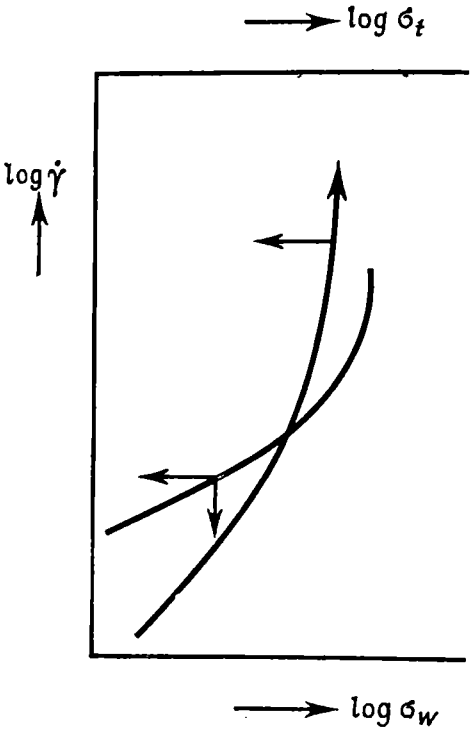

Fig. 10.11. Dependence of tangential stress and first-difference normal stresses on the shear rate

$$\gamma_e = \frac{\sigma_w}{2\sigma_t} \qquad (10.15)$$

$$G_e^0 = \frac{2\sigma_t^2}{\sigma_w} = \frac{2\eta_0\dot{\gamma}^2}{\sigma_w} \qquad (10.16)$$

$$\sigma_w = \frac{2\eta_0^2\dot{\gamma}^2}{G_e^0} = \xi_0\dot{\gamma}^2 \qquad (10.17)$$

where ξ is the coefficient of normal stresses. Equations (10.15)-(10.17) are strictly valid at shear stresses and shear rates which tend to zero. The initial maximum values of $\xi = \xi_0$ correspond to these conditions. However, experiment shows that Eqs. (10.15)-(10.17) are often valid in a rather wide range of low values of shear rates.

In the range of low shear rates, $\sigma_t \propto \dot{\gamma}$, while $\sigma_w \propto \dot{\gamma}^2$, i.e., normal stresses change with the shear rate more strongly than shear ones. As the shear rate increases, normal stresses grow slower and their dependence on the shear rate becomes weaker than quadratic. However, the growth of shear stresses with an increase in the shear rate is also retarded when non-Newtonian regimes are attained. Therefore, if the dependencies of shear and normal stresses on the shear rate are represented graphically in a way that the logarithmic scales of the quantities under consideration would be equal, we will obtain a picture which is schematically illustrated in Fig. 10.11. The flow curves and the plots of σ_w versus shear rate may intersect both in the region of the transition from the lower Newtonian branch to the structural branch, and on the structural branch of the flow curve. This intersection

is sometimes absent. The entire curve of the dependence of σ_w on the shear rate is then situated to the left from the flow curve.

We have seen earlier that viscosity which differs inconsiderably from its highest value is often exhibited in a rather wide range of low shear rates and stresses. At the same time, in these flow regimes, highly elastic deformation may have finite values, attaining tens of per cent, and this causes the orientation effect and its corresponding change in the polymeric structure. Consequently, change in the structure of a polymeric system cannot be determined by measuring only viscosity. Measurements of viscosity must be supplemented by a measurement of σ_w and γ_e, which in this case are parameters of greater sensitivity to the structure.

Since G_e^0 does not depend on M for polymers having a high molecular mass, ξ_0 is proportional to M^7 on the basis of Eqs. (10.10) and (10.17). Consequently, the initial value of the coefficient of normal stresses is the most sensitive parameter in the estimation of a change in the value of molecular masses.

The presence of highly elastic deformation in polymeric systems which are in a fluid state is very important. It determines the spontaneous change in the dimensions of specimens after deformation ceases, when stress which causes deformation either does not change at all or diminishes. Highly elastic deformation greatly affects the structure of a polymeric system, causing orientation effects which introduce ordering in the arrangement of long macromolecules.

10.9. DYNAMIC PROPERTIES AND RELAXATION SPECTRUM

Very important information on the mechanical properties and nature of polymeric systems in a fluid state is given by the dynamic methods of investigation, in which polymers are subjected to cyclic deformation. Usually, use is made of deformation (or loading) according to harmonic oscillatory regime, when deformation and stress change sinusoidally. In this case, the amplitude, i.e., the value of deformations, must be so small that the polymeric structure would not change. The time of cycles (periods T, i.e., quantities inverse to frequency ω) varies in a range of many decimal orders.

Apparently, the greater the number of deformation cycles per unit time, the higher is the deformation rate. Consequently, frequency has the same physical meaning as the deformation rate in a transient deformation regime. Indeed, liquid layers in laminar flow translate in the direction of shear with some difference in rates. Thus, each particle of a liquid is under the action of torque and therefore rotates continuously. Therefore, the frequency of

cyclic deformation and the shear rate are equal ($\omega = \dot{\gamma}$) for polymeric systems in a fluid state.

In dynamic measurements, determination is made of the energy which is stored in a polymer and is reversibly given off by it in every half-cycle (see Fig. 10.12*a*). A measure of this energy is the storage modulus of elastic deformation, or simply storage modulus G'. At the same time, the resistance of a polymer to deformation is determined which is caused by the dissipation of

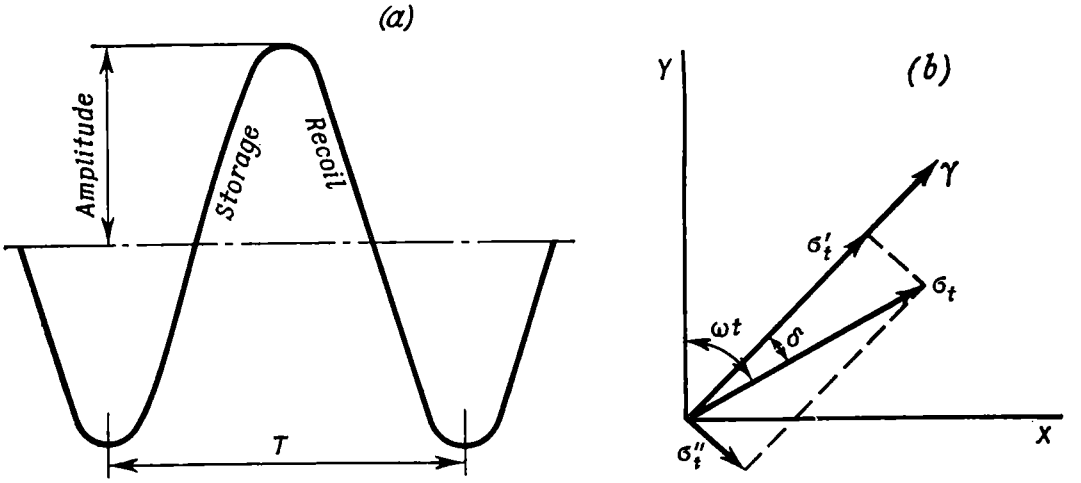

Fig. 10.12. Diagram of the storage and recoil of elastic energy at sinusoidal regimes of deformation of polymer systems (*a*) and vector diagram illustrating dissipative losses (energy scattering) in the case of the cyclic deformation of viscoelastic media (*b*)

energy, i.e., the conversion of a part of the work of deformation into heat in every cycle. This part of resistance of a body to deformation is characterized by the loss modulus G''. The ratio G''/G' is known as the mechanical loss tangent, $\tan\delta$, since it is precisely owing to the dissipative losses in each cycle that shift of deformation occurs relative to stress by a certain phase angle, and it is the greater, the higher are the losses. The loss modulus and the storage modulus have the same dimension, Nm^{-2}.

The foregoing is explained by a diagram (Fig. 10.12*b*) illustrating the position of the vector σ_t, which determines shear stress and moves with cyclic frequency ω. Time t corresponds to this position. As a result of losses owing to the convertion to heat — dissipation of work of external forces, deformation, represented by vector γ, lags behind stress by the value of the loss angle δ. The projection of vector σ_t on vector γ determines the stress which is in the same phase as deformation, and this is characteristic of the storage of elastic energy. The second component of vector σ_t characterizes dissipation. The determination of the moduli of storage,

losses and the mechanical loss angle follows from here:

$$G' = \sigma_t'/\gamma = (\sigma_t \cos\delta)/\gamma \tag{10.18}$$

$$G'' = \sigma_t''/\gamma = (\sigma_t \sin\delta)/\gamma \tag{10.19}$$

$$G''/G' = \tan\delta \tag{10.20}$$

The total resistance of a polymeric system to cyclic deformations is determined by both the storage of elastic energy and dissipative losses, and this is characterized by a complex modulus, which, consequently, depends also on both the storage modulus and the loss modulus. The absolute value of the complex modulus is $|G^*| = \sqrt{(G')^2 + (G'')^2}$. It has the dimension of $Jm^{-3} = Nm^{-2}$, i.e., the same as that of the storage and loss moduli. The complex modulus has the same physical meaning as shear stress at stationary flow of polymeric systems, because its value depends on the resistance of internal friction (dissipative losses) and resistance to the development of highly elastic deformation.

The meaning of the concept of viscosity in cyclic deformations is similar to that of viscosity which was discussed above for transient experiments, i.e., the absolute value of complex viscosity is numerically equal to the ratio of the absolute value of the complex modulus to cyclic frequency. It is similar to the relation $\eta = \sigma_t/\dot{\gamma}^0$. The concept of dynamic viscosity $\eta'' = G''/\omega$ is sometimes used. The quantities $|\eta^*|$ and η' have the same dimensions as the viscosity coefficient in Newton's equation.

Theory predicts and experiment confirms that there is a very important correlation between the parameters which are determined at dynamic and stationary flow regimes:

$$G'/\omega^2 = A_G^0 = 2\sigma_w/\dot{\gamma}^2 = 2\xi_0 \tag{10.21}$$

$$G_e^0 = \frac{2\eta_0^2}{\xi_0} = \frac{2\eta_0^2}{A_G^0} \tag{10.22}$$

where A_G^0 is the initial value of the elasticity coefficient. As we may see from the denotation, the relations (10.21) and (10.22) are strictly valid for ω and $\dot{\gamma}$ which tend to zero. At finite values of ω and $\dot{\gamma}$, these relations are valid in a range of frequencies and deformation rates which are the wider, the narrower is MMD for high-molecular linear polymers. In the case of monodisperse high-molecular polymers, they are valid in almost the entire range of shear rates up to spurt (p. 278). Dynamic measurements at sufficiently low frequencies make it possible to determine, in one experiment, the totality of the initial values of the most important rheological parameters.

Figures 10.13*a*, *b* show the dependencies of G' and G'' on ω for high-molecular ($M \gg M_{crit}$) linear polymers of narrow MMD (M_w, $M_n \leqslant 1.1$) at $T > T_g$. In the region of low frequencies, i.e., in the case of prolonged action of external forces, a large part of all the structural elements has time to relax, and therefore the storage modulus turns out to be small. In this case, $G' = A_G^0\omega$, and the curve $G'(\omega)$ rises steeply. The rate of its ascent then gradually slows down. The entire region of the growing values is known as the terminal region of the dependence $G'(\omega)$, since it relates to the slowest relaxation processes. It describes the properties of polymers in a fluid state.

When frequency increases (the duration of every deformation cycle decreases), an increasing number of structural elements do not have time to relax and the polymer passes over to the region of deformation effects, where there may be only rapid rearrangements of molecular conformations without a change in the relative position of their centres of gravity, i.e., polymer fluidity does not have time to exhibit itself. The plateau of high elasticity, i.e., the horizontal region on the curve $G'(\omega)$, corresponds to this state. Within every polymer homologous series, the height of the plateau does not depend on molecular mass and practically does not depend on temperature. The length of the plateau grows towards lower frequencies in proportion to $M^{3.5}$.

In the plateau region, polymers behave like cured systems. Indeed, the plateau of high elasticity of cured rubbers is only inconsiderably higher than that of uncured polymers, and this makes it possible to estimate the density of the spatial fluctuational network of these polymers in the same way as is done for cured specimens (p. 78). The density of the spatial network is determined by the molecular mass M_d of the chain segment between the nodes of a fluctuational network. The value of M_d may be calculated by using the equation $G' = (d\,RT)/M_d$. The segment of macromolecules that corresponds to M_d is known as the dynamic segment, because it is found by dynamic measurements.

The quantity M_d is connected with M_{crit}: for nonpolar polymers of the polyethylene type, $M_{crit} \simeq 2\,M_d$, and for weakly polar polymers (polymethyl methacrylate, etc.), $M_{crit} \simeq (3 \text{ to } 5)\,M_d$. At the value of $M \simeq (5 \text{ to } 7)\,M_d$, and inflection point appears on the dependence $G'(\omega)$ as the first indication of a rubber-like state. When $M \simeq (5 \text{ to } 10)\,M_d$, the plateau is clearly defined. The reduction parameter may be M_d, just as the expediency of reduction molecular masses by the value of M_{crit} was indicated above (p. 285).

The height of the plateau for various homologous series of linear polymers is within the limits of approximately a decimal, as is shown in Fig. 10.13.

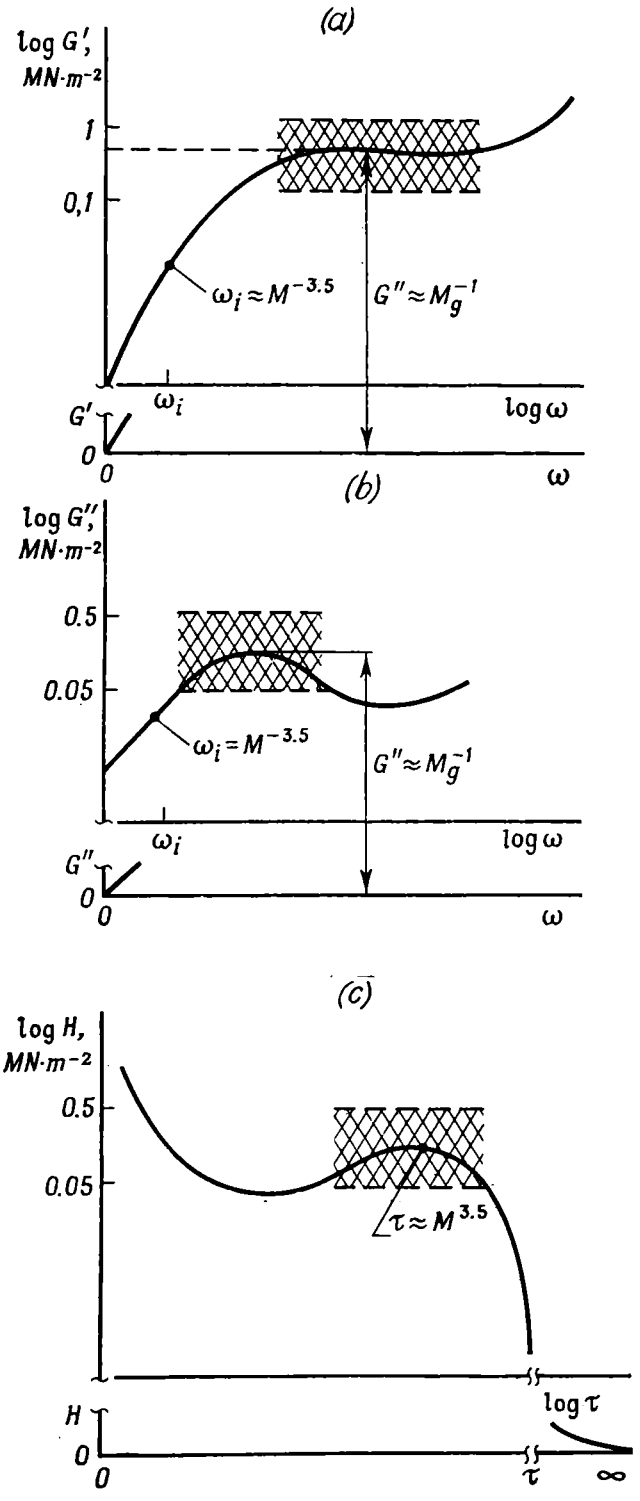

Fig. 10.13. Dependencies of the moduli of storage and losses on frequency in the case of the cyclic deformation (at sinusoidal regimes) of high-molecular polymers of narrow molecular-mass distribution. Spectra of relaxation times of such polymers

In the terminal zone of fluid and rubber-like states, the principle of temperature-frequency (time) equivalence is valid (p. 198), and high temperatures correspond to low frequencies, while low temperatures correspond to high frequencies.

Let us now consider the dependence $G''(\omega)$. At low frequencies, a large part of all the structural elements has time to relax during every cycle, and G'' is small; $G'' = \eta_0'\omega$, while $\eta_0' \simeq \eta_0$. The maximum of the dependence $G''(\omega)$ is attained with an increase in frequencies. This is a singular point which clearly characterizes the transition from a fluid to a rubber-like state. The maximum is determined by the superposition of losses which are caused by shifts of the centres of gravity of macromolecules and rapid conformation transitions which are typical of the rubber-like state.

The height of the maximum is simply connected with the height of the plateau, namely, $G''_{max} = 0.4G'_{pl}$, where G'_{pl} is the value of G' that corresponds to the plateau. With an elevation of temperature, when all relaxation processes proceed at higher rate, the terminal zones of the curves $G'(\omega)$ and $G''(\omega)$ shift towards higher frequencies according to the same law that governs the change in initial viscosity with temperature. As the molecular mass grows, these curves shift towards lower frequencies so that $\omega_j \propto M^{-3.5}$. The rise in the curves of $G'(\omega)$ and $G''(\omega)$ in the high frequency range corresponds to a transition to the glassy state of polymers.

As MMD widens, the regions of proportionality of G' and G'' to ω^2 and ω, respectively, shift towards lower frequencies. The transition from the terminal zone to the plateau zone covers an ever growing frequency range, the plateau slants, while the maximum on the curve $G''(\omega)$ becomes less defined.

Various structural elements in polymeric systems spontaneously rearrange in different periods of time under the action of thermal motion. Thus, there is a set of relaxation times that determines the ability of all structural elements to undergo rearrangement. Some of these relaxation times are encountered frequently, while others less so. The intensity of exhibition of relaxation time with respect to other times is represented by a function of their distribution H. It determines the relaxation spectrum of a polymeric system, which is calculated by the dependencies $G'(\omega)$ and $G''(\omega)$. Figure 10.12*c* shows a typical relaxation spectrum of a polymer of narrow MMD that corresponds to data in Fig. 10.12*a* and *b*. In the transition to wide MMD, the terminal spectrum zone, which corresponds to great relaxation times and describes the behaviour of a polymer as a fluid system, expands over a large time interval, and the maximum turns out to be less clearly defined.

Dynamic measurements make it possible to determine, by means of frequency and temperature scales, the length of the zone of

transition from a fluid state to a rubber-like state and the zone of transition from this state to a glassy one. The length of the zone of a rubber-like state is determined in this way. The dynamic method is the strictest variant of the thermomechanical investigation of polymers. Relaxation (including glass-transition temperature) and phase transitions are determined by dynamic measurements. Such measurements are made in a wide temperature range at low frequency, when a considerable part of relaxation processes has time to occur. An indication of a relaxation transition, and also of phase transitions, is the presence of the maximum in dependence of $\tan\delta$ on temperature, because, in the course of phase and relaxation transitions from one state to another, rearrangement of a system occurs, when losses typical of both states are summed up. The dynamic method is very convenient for estimating the curing and vulcanization of polymers; the expansion of the high-elasticity zone and a decrease in losses in the low-frequency zone correspond to this.

It is important to note that the dynamic characteristics of the mechanical properties of polymers are in many respects similar to their dielectric characteristics (see Chap. 11).

10.10. EXTENSION

Polymers in a fluid state are often subjected to extension deformations. This is encountered in the production of fibres, films and other articles. The simplest type of extension is uniaxial deformation. The value of deformation is defined in this case as the relative elongation of a specimen in the direction of extension. When its length changes from initial l_0 to a given l, deformation

$$\varepsilon = \int_{l_0}^{l} \frac{dl}{l} = \ln \frac{l}{l_0} \tag{10.23}$$

where $l/l_0 = \alpha$ is the extension ratio. If l differs inconsiderably from l_0, then l/l_0 is close to unity. Then, confining ourselves to the first term of expansion for the logarithmic function, we obtain $\varepsilon = \frac{l - l_0}{l} = 1 - \alpha$. When bodies exhibiting rubber-like properties are subjected to extension deformation, total deformation ε_{tot} consists of highly elastic deformation ε_e and irrecoverable deformation of flow ε_f, i.e.,

$$\varepsilon_{tot} = \varepsilon_e + \varepsilon_f = \ln \frac{l_{st}}{l_0} + \ln \frac{l}{l_{st}} \tag{10.24}$$

where l_{st} is the length of a specimen after elastic recovery, i.e., the length which takes account of the storage of irrecoverable deformation in it.

The extension deformation rate $d\varepsilon/dt = \dot{\varepsilon}$ (its dimension is s^{-1}) is known also as the longitudinal gradient of velocities, because it is determined by the drop in the linear rate of movement of the adjacent layers in a sample. The force which causes the extension of the sample divided by its cross-sectional area determines acting normal stress P.

The extension of liquids was first studied by Trouton at the beginning of this century for very viscous substances (resins), which do not exibit high elasticity. By analogy with Newton's equation [Eq. (10.1)], he wrote the relation between the deformation rate (longitudinal velocity gradient) and normal stress as the following equation:

$$P = \lambda\dot{\varepsilon} \qquad (10.25)$$

where λ is the proportionality factor called longitudinal (extensional) viscosity. Its dimension is the same as that of the viscosity coefficient in Newton's equation. Trouton found that $\lambda = 3\eta$.

For viscoelastic media, Eq. (10.25) and the foregoing relationship between longitudinal and shear viscosities are strictly valid at stresses tending to zero. Viscosity which meets this condition is known as initial viscosity (λ_0). In practice, the constancy of longitudinal viscosity, i.e., its equality to the value of λ_0 for linear high polymers, is satisfied in a range of stresses and rates of deformation which is the wider the narrower is MMD. The energy of activation of polymer flow in the field of the longitudinal velocity gradient does not differ from its value for shear.

Under stationary conditions of flow, $\varepsilon_e = \text{const}$. Its value is determined, in conformity with Eq. (10.24), by the ratio l_{st}/l_0 and, consequently, by the length of a specimen after elastic recovery. Since, under stationary conditions, $\dot{\varepsilon}_e = 0$, then $\dot{\varepsilon}_f = \dot{\varepsilon}_{tot}$. Highly elastic deformation changes during the transition from rest state to stationary flow, or, in general, from one regime of deformation to another. Then, in order to determine longitudinal viscosity at every given instant of time, it is necessary to know the respective values of stress and of the rate of storage of irrecoverable deformations. The quantity $d\varepsilon_f/dt$ is found from the time dependence of residual deformation. To this end, it is necessary to carry out a series of tests in which deformation is interrupted at various instants and residual deformation is measured after every interruption. Since this is very laborious, only the rate of total deformation is often determined from its dependence on time.

The simplest in the case of deformation is the behaviour of high-molecular linear polymers of narrow MMD. In extension, this is schematically illustrated in Fig. 10.14 for $T > T_g$. It shows the deformability of polymers depending on $\dot{\varepsilon}$ and $\dot{\varepsilon}a_T$, where a_T is the temperature reduction coefficient (p. 199). The dependencies re-

presented in Fig. 10.14 are then temperature invariant. At deformation rates lower than the critical one, which correspondes to the dashed vertical line, the stationary flow regimes with viscosity equal to its initial value can be realized. A definite value of quasi-equilibrium highly elastic deformation, which grows with the deformation rate, corresponds to each such regime.

For high-molecular samples with narrow MMD, there is a simple relation between the critical regimes of extension and shear, namely, $P_c = 3\sigma_{tc}$, where σ_{tc} corresponds to the spurt phenomenon.

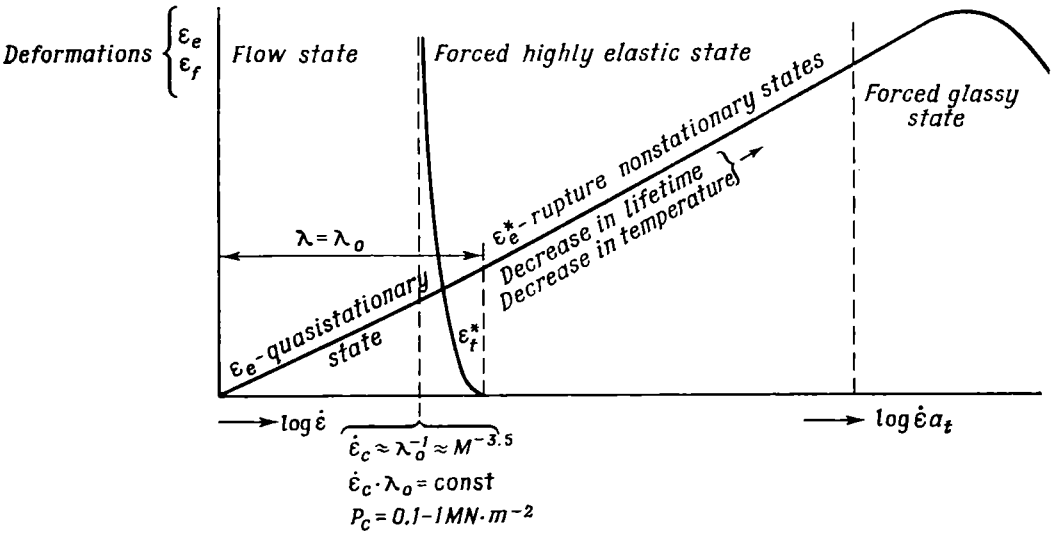

Fig. 10.14. Most important characteristics of the deformation behaviour of linear flexible-chain high-molecular polymers of narrow distribution in a very wide range of deformation rates in the case of extension

When the critical deformation rate is attained, a transition is made from a fluid state to a rubber-like state, and the ability of polymers to store up irrecoverable deformation sharply drops. This is shown in Fig. 10.14 by the steeply dropping curve ε_f^*. Deformability is always limited in the region of forced high elasticity. Stationary deformation regimes cannot be realized in this state, and the extension process ends in the rupture of samples. Therefore, each point on the dependencies of deformations and stresses on the deformation rate corresponds to the test of a separate sample, and this differs considerably from conditions under which polymers in a fluid state are tested, when all the regimes can be realized on one sample.

In the case of polymer extension, when $P > P_c$, characteristic parameters are both the maximum, highest values of stresses (ultimate strength) and of recoverable deformations, and the time taken from the beginning of deformation to the rupture (lifetime) of samples, i.e., rupture characteristics. As the deformation rate

increases, ultimate strengths and rupture deformations grow, while lifetime rapidly decreases. Depending on the preset rates of deformation or stresses, ultimate strength ranges from decimals to 5-10 MNm^{-2}, ultimate deformations may reach several hundreds of per cent, and lifetime changes from many hours to small fractions of a second. The relation between ultimate strength and lifetime (time prior to rupture) is determined by a power equation, i.e., just in the same way as for cured rubbers. The effect of temperature on rupture characteristics is determined by its effect on initial viscosity. This unequivocally shows that, in a forced rubber-like state, the strength properties and the process of the rupture of polymers are determined by their relaxation characteristics. In contrast to what is known for crystal and glassy polymers in a forced rubber-like state, the process of the rupture of macromolecules, the formation of free radicals and the corresponding decrease in molecular mass are of little importance.

When the deformation rate grows considerably, polymers pass over from a rubber-like to a forced glassy state, which corresponds to the maximum of highly elastic deformation. The greatest, by the order of magnitude, deformability of macromolecules, i.e., the ratio of their contour length to the square root from the root-mean-square end-to-end distance of macromolecules, corresponds to this transition. After passage to a glassy state, ultimate strength continues to grow, but at the same time the brittleness of polymers begins to be more pronounced: their deformability decreases, the process of macromolecular rupture plays an ever greater role, and the temperature-time superposition principle is no longer valid.

In polymolecular polymer samples, high-molecular fractions are in the solution of fractions of lower molecular mass. As the deformation rate increases, highly elastic deformation may grow very sharply without the rupture of a sample, because the remaining part of a polymer is still in a fluid state. This causes greater compliance with the broadening of MMD and leads to the fact that the transition of polymers from one state of aggregation to another extends over wide ranges of the rates of deformation and stresses, and fluidity decreases slower as deformation rates increase. Beyond the limits of very low deformation rates, the relation between uniaxial extension and simple shear becomes very complex.

A considerable uncoiling high-molecular macrochains in polymolecular samples, on the one hand, increases their rigidity, facilitates orientation towards deformation and may intensify intermolecular interaction, and on the other hand, reduces the density of the spatial network. The rate of growth of stresses relative to the deformation rate may either increase (viscosity grows) or decrease (viscosity diminishes), depending on the composition of polymers and deformation regimes. That is what considerably distinguishes

extension from shear, where the determining factor is the action of the torque of forces in adjacent layers, and this causes the rotation of macromolecules and, consequently, the breakdown of the spatial network and the diminution of viscosity.

Although viscosity may decrease or increase under the action of extension, an increase in it is observed more often.

Figure 10.15 shows a change in longitudinal viscosity in the transition from rest to stationary flow. Viscosity grows linearly

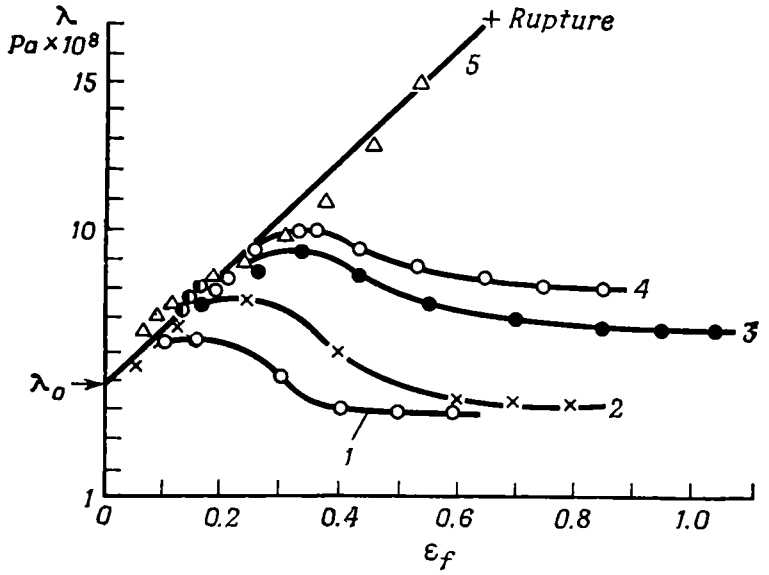

Fig. 10.15. Change in longitudinal viscosity at various rates for polystyrene of wide molecular-mass distribution. Deformation rates: 0.137, 1.11, 2.98, 4.5, 5.7 s^{-1} (temperature 130 °C)

with an increase in deformation during the initial period of deformation, when the development of highly elastic deformation and the orientation effect are the determining factors. On further deformation, the spatial network of macromolecules breaks down, causing the appearance of a maximum and then a decrease in viscosity to a constant which corresponds to the conditions of stationary flow. But it follows from the figure that this decrease in viscosity does not compensate its growth at the initial stage of deformation. The higher the deformation rate, the greater is the total increase in viscosity. At high deformation rates, highly elastic deformation develops very intensively and the orientation effect becomes so strong that flow slows down and a polymer ruptures.

10.11. BULK COMPRESSION

The compressibility of polymers is much higher than that of low-molecular liquids. A pressure above 500-1000 Pa may have a considerable effect on the properties of polymers. When pressure in-

creases, the fluid-state region shifts towards higher temperatures; temperature may rise by tens of degrees.

Under bulk compression, polymers behave like viscoelastic bodies. This means that, at preset pressure or a definite degree of compression, the equilibrium state is reached in finite, sometimes comparatively large, intervals of time (minutes or even tens of minutes). Therefore, the compressibility of polymers decreases with an increase in the rate of volume strain.

An increase in pressure causes a decrease in free volume in polymers. This becomes significant at pressures above 400-600 Pa, when a considerable increase in viscosity is observed. As pressure increases further, viscosity grows sharply, depending exponentially on pressure: $\eta \approx e^P$. When pressure rises to 2000-3000 Pa, viscosity grows by tens of times.

The effect of pressure on viscosity is the most pronounced in the region of Newtonian flow, where $\eta = \eta_0$. At this flow regime, the piezo viscosity coefficient $(d\eta/\eta)/dP$ has the highest value and does not depend on whether it is measured at constant stresses or at constant shear rates. Conversely, the value of the piezo coefficient of apparent viscosity depends on the conditions of its determination. Piezo coefficients measured at various constant shear stresses differ little from one another, but piezo coefficients determined at different constant shear rates depend on the values of the latter, decreasing as they grow. Therefore, the piezo coefficients of apparent viscosity at constant shear stresses may be higher than at constant shear rates. Accordingly, viscosity measured at high pressures and constant shear stresses may be much higher than its value at a constant shear rate. Thus, there is a qualitative analogy between the dependence of apparent viscosity on temperature, on the one hand, and pressure, on the other.

The effect of pressure on viscosity decreases with an elevation of temperature and increases with a growth in macromolecular branching.

The phenomena observed in polymers in the fluid state at high pressures have been studied very little.

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CHAPTER 11

Electrical Properties of Polymers*

The use of polymers in engineering as dielectrics is becoming increasingly important. Choice of the polymeric dielectric for each concrete case depends on its dielectric and other physical properties over a wide range of temperatures and electric field frequencies. However, the dielectric properties of polymers are tested not only for engineering purposes. Investigation of dielectric properties is one of the most convenient and sensitive methods of studying polymer structure.

11.1. ELECTRICAL PROPERTIES OF DIELECTRICS

The basic electrical properties of dielectrics are volume resistivity, electric strength (dielectric breakdown strength), permittivity or dielectric constant, and dielectric loss. The choice of dielectric for each particular purpose is determined by the temperature and electric field frequency dependencies of these quantities.

Volume resistivity or its reciprocal, *volume conductivity*, depends on the presence of free charges (electrons or ions) and their mobility. A dielectric usually contains very few free charges, and therefore has a low conductivity (of the order of 10^{-19} to 10^{-13} ohm$^{-1}\cdot$cm^{-1}). With rising temperature the conductivity of a dielectric increases owing to increasing mobility of the free charges.

Electric strength. Within the field intensity range of 10^5-10^6 V/cm the conductivity of a dielectric increases at constant temperature with increasing electric field intensity. After a certain potential difference is reached between the electrodes further increase of the

* Chapter 11 was written by T. I. Borisova and L. L. Burstein and edited by G. P. Mikhailov.

conductivity will sharply increase the current passing through the dielectric, i.e., will cause dielectric breakdown. The material loses its dielectric properties, becomes a conductor and fails. The electric field intensity at which breakdown occurs (E_b) is the measure of *electric strength* of the dielectric.

The *permittivity* or *dielectric constant* of a substance (ε') is defined as the ratio of the capacity of an electric capacitor filled with the substance to that of the same capacitor in vacuum, at a definite external field frequency.

Dielectric loss is the part of the energy of an electric field that is dissipated irrecoverably as heat in the dielectric.

Real permittivity is associated with the process of polarization, i.e., with the development of a definite electric moment in unit volume of the dielectric when it is placed in an electric field. The electric moment per unit volume equals the geometrical sum of the moments of the dipoles contained in the volume in question. Dipoles may be *constant* (*permanent*) or *induced* *.

A molecule possesses a constant dipole moment if the centres of gravity of its positive and negative charges are displaced relative to each other. Such a dipole exists even in the absence of an electric field.

Constant dipoles are characterized by the value of their permanent dipole moment, equal to the product of the magnitude of the charges and their separation:

$$\mu_0 = ql \tag{11.1}$$

In liquids and gases dipole molecules are arranged randomly owing to thermal motion. In an electric field the dipole molecules orient themselves predominantly in the direction of the field (the potential energy of the dipole then becomes a minimum) and the total electric moment of all the dipoles differs from zero, resulting in what is known as an *orientation moment.*

Induced dipoles arise only if the dielectric is placed in an electric field. Under the influence of the latter the charges in the nonpolar dielectric molecules are displaced and their distribution becomes asymmetric, i.e., induced dipoles appear. The moment m of each of these dipoles is proportional to the intensity of the applied field E:

$$m = \alpha E \tag{11.2}$$

where α is a proportionality coefficient called *polarizability.*

If there are n molecules in unit volume, the electric moment I of unit volume equals

$$I = nm = n\alpha E \tag{11.3}$$

* According to this feature dielectrics are divided into polar and nonpolar, though such a classification is arbitrary.

An electric moment arising from displacement of charges is called a *deformation moment.* It may appear as a result of deformation of electron shells and/or a shift of atomic nuclei.

The total electric moment of a dielectric I (or the total polarization P) is the sum of the orientation and deformation moments

$$I = I_{or} + I_{def} \tag{11.4}$$

The moment caused by elastic deformation of electron shells or by elastic shift of the atoms constituting a molecule is established almost instantaneously (in a matter of 10^{-13} or 10^{-14} s). The dielectric constant associated only with establishment of an electric moment of this kind is determined by the commonly known Maxwell relation $\varepsilon' = n^2$ (n being the optical refractive index). This is the main type of polarization in nonpolar dielectrics.

The orientation part of the total electric moment, which is predominant in polar dielectrics, is established much more slowly, the time needed for this depending on the temperature, which determines the intensity of molecular movement. With increasing temperature the mobility of the molecules increases, and therefore orientation of polar molecules in the direction of the external electric field is faster.

On the other hand, the thermal motion of the dipoles increases, and this disturbs their orientation, so that the orientation moment decreases with rising temperature.

If the external electric field is variable, the orientation moment depends on the ratio between the field frequency ω and the relaxation time (Chap. 7) of the orientation moment of the dielectric in question, i.e., on the rate of recovery of the statistically equilibrium arrangement of molecules.

As is known, relaxation time varies with temperature according to an exponential law (p. 190). If the sample temperature is not high enough (τ is large) or the period of application of the field is too short (high ω), i.e., $\omega\tau \gg 1$, the orientation moment will not have time to develop and the dielectric will behave like a nonpolar one; only a deformation moment will be observed. At high temperatures and low frequencies, when $\omega\tau \ll 1$, the orientation moment is fully established at each instant and reaches its maximum static value.

In the temperature-frequency range where $\omega\tau \approx 1$, there is a phase shift between the voltage applied at any given instant and the orientation moment, or more precisely the electric displacement vector, as a result of which the moment lags somewhat behind the applied voltage. This phase shift is a result of dissipation of part of the energy as heat. It is customary to characterize phase shift by the angle δ. Since the energy dissipated per unit volume of dielectric as heat (dielectric loss) is proportional to the field fre-

quency and to tan δ, the angle δ is usually called the *loss angle.*

Besides tan δ, dielectric loss is characterized by the *loss factor* * $\varepsilon'' = \varepsilon' \tan \delta$, where ε' is the permittivity of the material.

For convenience in mathematical treatment the concept *complex permittivity* ε was introduced, this being a complex function of ε' and ε'':

$$\varepsilon = \varepsilon' + i\varepsilon'' \tag{11.5}$$

where $i = \sqrt{-1}$.

If the orientation moment in an electric field is established by an exponential law, the real and imaginary parts of complex permittivity, ε' and ε'', respectively, can be expressed as follows:

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \tag{11.6}$$

$$\varepsilon'' = (\varepsilon_0 - \varepsilon_\infty)\frac{\omega\tau}{1 + \omega^2\tau^2} \tag{11.7}$$

where ε_0 = permittivity at $\omega = 0$, i.e., in a constant field (*static permittivity*)

ε_∞ = permittivity in a field of infinitely high frequency.

The relationship between the complex permittivity ε, polarization P, field frequency ω, and relaxation time τ per mole of a polar gas is given by the equation

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} \cdot \frac{M}{d} = \frac{4}{3}\pi N_A \left[\alpha + \frac{\mu_0^2}{3kT(1 + i\omega\tau)}\right] \tag{11.8}$$

where M = molecular mass

d = density

N_A = Avogadro's number

α = polarizability

μ_0 = permanent dipole moment.

It is evident from equation (11.8) that only the orientation polarization (second term) depends on the field frequency and relaxation time. At $\omega\tau \gg 1$ the second term of the equation becomes negligibly small (the denominator being very large). Then the total polarization equals the deformation polarization $P = 4/3\pi N_A\alpha$ and $\varepsilon = \varepsilon_\infty = n^2$, where n is the refractive index.

At $\omega\tau \ll 1$ the total polarization is given by the equation:

$$P = \frac{4}{3}\pi N_A \left(\alpha + \frac{\mu_0^2}{kT}\right) \tag{11.9}$$

The permittivity then reaches its maximum static value ε_0.

At $\omega\tau = 1$ an inflexion point appears on the ε' vs. log ω curve and a maximum, on the ε'' vs. log ω (or tan δ vs. log ω) curves

* Also known as the *imaginary part of complex dielectric permittivity* [see Eq. (11.5)].

(Fig. 11.1*a*). The temperature dependencies of ε' and ε'' (or $\tan\delta$) are of a similar nature (Fig. 11.1*b*).

The position of this maximum depends on the temperature and the applied frequency; the higher the temperature, the more is the maximum shifted towards high frequencies (and with increasing frequency, towards higher temperatures).

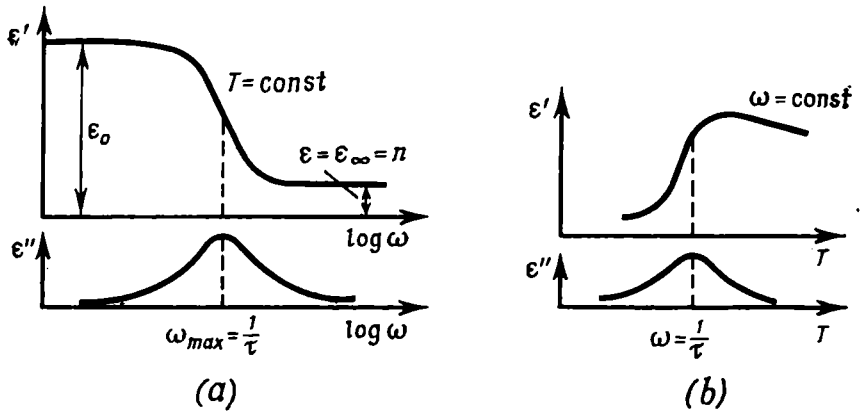


Fig. 11.1. Diagrams of dependencies of ε' and ε'' on electric field frequency (*a*) and temperature (*b*)

The dielectric loss or the energy W dissipated as heat per unit volume of a nonpolar dielectric is given by the formula

$$W = \frac{\varkappa E^2}{8\pi} \tag{11.10}$$

where $\varkappa$ = conductivity of the dielectric determined by the residual current in a constant electric field

E = field strength or intensity.

It is evident from the equation that the energy dissipated in a nonpolar dielectric is independent of the field frequency, and since $\varkappa$ has very low values, the value of W is not high according to Eq. (11.10).

The electromagnetic field energy dissipated as heat per unit volume of a polar dielectric is proportional to the loss factor $\varepsilon' \tan\delta$, squared field strength E^2 and frequency ω of the applied field:

$$W = \frac{\omega E^2}{8\pi} \varepsilon' \tan\delta \tag{11.11}$$

In the low frequency region the energy dissipation in a nonpolar dielectric is relatively small, but the amount of dissipated energy increases rapidly with increasing frequency. This accounts for the great importance of the $\tan\delta$ value and its variation with temperature and frequency, especially when choosing dielectrics for high-frequency use.

11.2. ELECTRICAL PROPERTIES OF POLYMERS

Electrical Conductivity. The electrical conductivity of a polymer $\varkappa$ depends on the presence of free ions not connected chemically with the macromolecules.

The molecular chain proper does not participate in the transfer of electric charges. Therefore the conductivity of polymers depends largely on the presence of low-molecular impurities that can serve

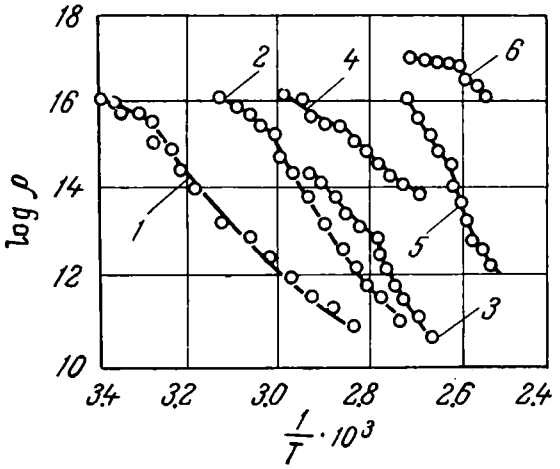


Fig. 11.2. Temperature dependence of resistivity ρ of some polymers:
1—poly(vinyl acetate); *2*—poly(vinyl butyral); *3*—poly(vinyl formal); *4*—poly(vinyl methacrylate); *5*—poly(vinyl ethylal); *6*—polystyrene

as sources of ions. The chemical constitution has only an indirect effect on the mobility of the ions.

In the glassy state the conductivity of polymers is approximately 10^{-13} to 10^{-19} ohm$^{-1}\cdot$cm^{-1}. With increasing temperature the conductivity of polymers increases according to an exponential law:

$$\varkappa = Ae^{-\Delta U/RT} \qquad (11.12)$$

where A = coefficient weakly dependent on temperature $\left(A \propto \frac{1}{T}\right)$

R = universal gas constant

ΔU = activation energy, i.e., energy difference between the active and the initial state of ions.

At a temperature above the glass-transition temperature ionic mobility increases owing to the considerable mobility of the chain units, and the conductivity rises.

The temperature dependence of resistivity of polymers is illustrated by Fig. 11.2.

Dielectric Breakdown Strength. It has been established experimentally that polymers containing no polar impurities possess high

dielectric strength. Their breakdown strength at room temperature is between 10^6 and 10^7 V/cm, the higher values pertaining to polymers containing polar groups. The breakdown strength of a given polymer may be much lower if the material contains moisture or air inclusions, which ionize in a strong electric field.

Permittivity and Dielectric Loss. A characteristic feature of polymers is independent movement of chain sections consisting of a large number of monomeric units (segments).

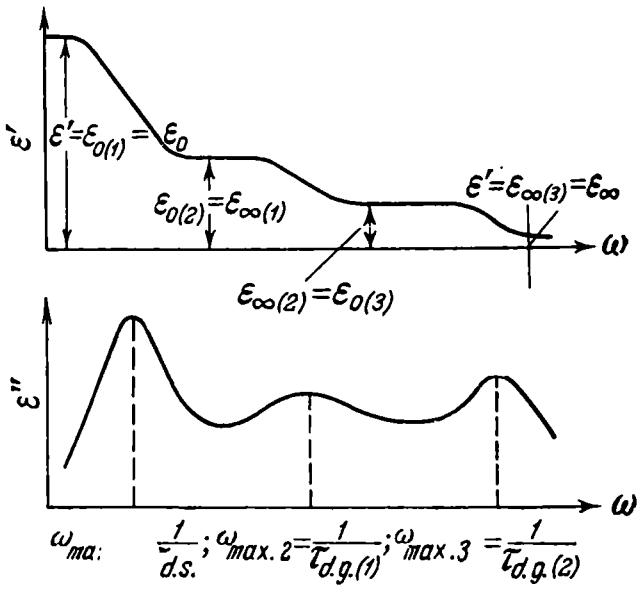


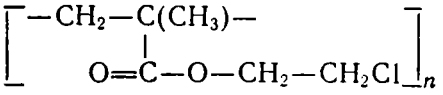
Fig. 11.3. Dependence of ε' and ε'' on electric field frequency for polymers with one region of dipole-segmental losses (d. s.) and two regions of dipole-group losses (d. g.)

Besides segments, smaller and more mobile kinetic units are also moving in polymers. Such kinetic independent units may be side chains or individual atomic groups, e.g., polar substituents. The relaxation time of the orientation moment of such groups is smaller than the relaxation time of main-chain segments, and for this reason they can retain their mobility at lower temperatures, where the segments of the main chain are practically immobile.

If a polymer containing polar groups is placed in an electric field, orientation of its segments and smaller kinetic units will be observed at definite relaxation time to field frequency ratios, and this gives rise to definite values of dielectric constant and dielectric loss. Within the frequency and temperature interval corresponding to the condition $\omega\tau = 1$ the ε'' vs. ω curves pass through a maximum, and an inflexion point appears on the ε' vs. ω curves (Fig. 11.3).

Two types of dielectric loss have been established for all polymers. The first type of dielectric loss, called *dipole-segmental* *, is associated with orientation rotation of the polar units of the macromolecule under conditions where segmental movement is possible, i.e., in the rubber-like state (above the T_g of the polymer). The second type, called *dipole-group* **, is due to orientation of the polar groups themselves. Losses of this kind may also occur below the T_g of the polymer, i.e., in the glassy state, and above T_g, i.e., in the rubber-like state.

If there are polar groups in the polymer side chain, capable of orientation in an electric field independent of one another and having different relaxation times, two dipole-group loss maxima will appear on the tan δ vs. temperature or tan δ vs. frequency curves. For example, the side chains of poly(β-chloroethyl methacrylate)



contain the polar bonds C=O and C—Cl, separated by one methylene group. One dipole-group loss maximum is due to the mobility of the C—Cl dipole, and the other, to the presence of the polar C=O group. Both kinds of losses depend on the applied field frequency. With increasing frequency the position of the tan δ maximum shifts towards higher temperatures.

Figure 11.3 shows the ε' and ε'' vs. field frequency dependencies characteristic of polymers displaying one dipole-segmental and two dipole-group loss regions. Equations 11.6 and 11.7 describe the frequency dependencies of ε' and ε'' in each of the regions of dipole losses of real polymers only approximately. Usually the ε' vs. ω curve has a smaller declivity than would be expected according to formula (11.6), and the values of ε'' are lower and the ε''_{max} region is drawn out over a larger range of frequencies than formula (11.7) predicts, and this region may be unsymmetrical. The discrepancy between formulas (11.6) and (11.7) and the actual behaviour of polymers can be eliminated more or less by introducing a set of relaxation times. Then τ in the condition $\omega\tau = 1$ is understood as the most probable relaxation time. The high-frequency value of the dielectric constant ε_∞ is 2.2 to 2.5 for all polymers. The static quantity ε_0 may have a wide range of values depending on the polymer structure. Thus, in the case of polyethylene $\varepsilon_0 = 2.25$, and for poly(methyl methacrylate) at 140 °C $\varepsilon_0 = 5$.

* Dipole-segmental loss is often denoted by the letter α.

** Dipole-group loss is denoted by the letters β, γ, δ, etc., depending on the mechanism of loss.

The values of tan δ_{max} of dipole-segmental and dipole-group losses of some polar and nonpolar polymers are listed in Table 11.1.

TABLE 11.1. *Values of tan δ_{max} of Dipole-Segmental and Dipole-Group Losses of Some Polar and Nonpolar Polymers (at 10^3 cps)*

Polymer	Dipole-segmental loss	Dipole-group loss
Polystyrene	3×10^{-4}	—
Polyethylene	3×10^{-4}	—
Poly(vinyl carbazole)	1×10^{-3}	—
Poly(vinyl acetate)	3×10^{-1}	2×10^{-3}
Poly(methyl methacrylate)	3×10^{-2}	7×10^{-2}
Poly(ethyl methacrylate)	8×10^{-2}	6×10^{-2}
Poly(isopropyl methacrylate)	8×10^{-2}	2.5×10^{-2}
Poly(methyl acrylate)	10×10^{-2}	2.7×10^{-2}
Poly-*p*-chlorostyrene	5×10^{-1}	—
Poly(β-chloroethyl acrylate)	9×10^{-2}	4×10^{-2}
Poly(β-chloroethyl methacrylate)	7×10^{-2}	3×10^{-2}; 1×10^{-2}

It is evident from Table 11.1 that the lowest values of tan δ_{max} are those of the nonpolar polymers polyethylene and polystyrene, which are high-frequency polymeric dielectrics.

11.2.1. Relaxation Time and Its Temperature Dependence

Investigation of the temperature-frequency dependence of the dielectric loss factor enables an estimate of the relaxation time of the orientation moment in the rubber-like and glassy states.

Making use of the relation

$$\omega_{max}\tau = 2\pi f_{max}\tau = 1 \qquad (11.13)$$

(where f_{max} is the linear field frequency at which ε'' passes through a maximum at constant temperature), the relaxation time τ corresponding to a kinetic unit can be determined directly from the ε'' vs. ω curve. Low-molecular liquids and dilute polymer solutions show the shortest relaxation times of dipole polarization. Thus, at 50 °C the relaxation time τ of propyl and isobutyl alcohols is 2×10^{-10} s, and that of glycerol is 6×10^{-7} s.

Large relaxation times are characteristic of dipole-group losses in polymers, and still higher ones, of dipole-segmental losses. Thus, at a temperature about 50 °C below T_g the dipole-group loss relax-

ation time of poly(methyl methacrylate) is 6×10^{-4} s, that of poly(isopropyl methacrylate), 2×10^{-3} s and of poly(methyl acrylate), 2×10^{-7} s. The relaxation time of dipole-segmental losses at a temperature close to T_g is of the order of 10^{-1} s. With increasing temperature τ decreases. At 50 °C, i.e., at a temperature 43 °C above the T_g of poly(methyl acrylate), the relaxation time of dipole-segmental loss is 2×10^{-5} s.

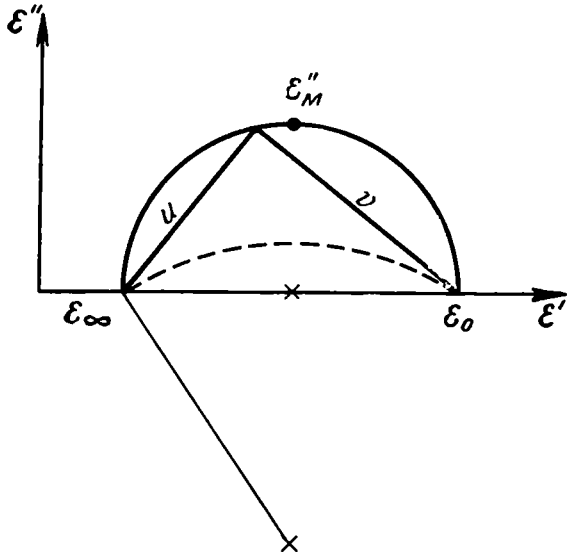


Fig. 11.4. Circle diagram (explained in the text)

Relaxation time determined by Eq. (11.13) is the average, or the *most probable*, relaxation time, because actually every polymer has a set or spectrum of relaxation times that is determined by a set of structural units of different mobility.

One of the ways of taking account of the spectrum of relaxation times is by plotting the so-called circle diagram. To this end, the dependence of ε'' on ε' is represented by a semicircumference with radius R and the centre lying on the abscissa axis and having coordinate a (Fig. 11.4):

$$x = \varepsilon'; \quad y = \varepsilon''; \quad R = \frac{\varepsilon_0 - \varepsilon_\infty}{2}; \quad a = \frac{\varepsilon_0 + \varepsilon_\infty}{2}$$

Thus, the circumference equation may be written as follows:

$$\left(\varepsilon' - \frac{\varepsilon_0 + \varepsilon_\infty}{2}\right)^2 - \varepsilon''^2 = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{2}\right)^2$$

For every point of the circumference, the ratio $\frac{\varepsilon''}{\varepsilon' - \varepsilon_0}$ is a constant equal to $\omega \cdot \tau$. This can be easily shown by dividing Eq. (11.7) by Eq. (11.8). On the other hand, $\frac{\varepsilon''}{\varepsilon' - \varepsilon_0} = \frac{u}{v}$ (Fig. 11.4).

Consequently, when this ratio is determined and when the frequency at which the values of ε' and ε'' are determined is known, τ can be calculated by equation $\omega\tau = \frac{u}{v}$. But the value calculated in such a way is valid only for one relaxation time. In reality, Eqs. (11.7) and (11.8) describe the dependencies of ε' and ε'' on frequency in every region of dipole losses of real polymers only approximately. Usually, the relation $\varepsilon' = f(\omega)$ is more sloping than it should be according to formula (11.7), the values of ε'' in the maximum are lower, and the ε_{max} region is drawn out over a larger frequency range than formula (11.8) predicts, and it may be unsymmetrical. Circle diagrams assume the form of a segment of a circle which is often distorted, the centre of the circumference that corresponds to it lying below the axis of abscissas. The discrepancy between formulas (11.7) and (11.8), on the one hand, and the real behaviour of polymers, on the other, is eliminated to a certain extent by introducing a set of relaxation times into the consideration. The angle $\frac{2\pi}{2}$, formed by a segment which connects the circumference centre with the point of intersection of an arc diagram with ε'-axis, is a measure of the width of the spectrum of relaxation times. The parameter of distribution of relaxation times α may assume values ranging from zero to unity, the value of $\alpha = 0$ corresponding to formulas (11.7) and (11.8), i.e., to the case of a single relaxation time, while $\alpha = 1$ to an infinitely wide set of relaxation times.

By studying the temperature-frequency dependence ε'', we can calculate the activation energy of dielectric polarization ΔU_{dip} by the equation

$$\tau = \tau_0 \cdot e^{\frac{\Delta U_{dip}}{RT}} \tag{11.14}$$

After taking the logarithm of Eq. (11.14), we obtain

$$\log \tau = \log \tau_0 + \frac{\Delta U}{2.303R} \cdot \frac{1}{T} \tag{11.15}$$

or, according to Eq. (11.13),

$$\log f_{max} = \log \frac{1}{2\pi\tau_0} - \frac{\Delta U}{2.303R} \cdot \frac{1}{T} \tag{11.15a}$$

The calculation of ΔU_{dip} is performed in the following way: the most probable relaxation time for several temperatures is determined and the graph of dependence of $\log \tau$ or $\log f_{max}$, which corresponds to $\omega\tau = 1$, on inverse temperature is plotted. According to Eqs. (11.15) and (11.15a), these dependencies should be expressed by straight lines, and this is usually observed for a narrow temperature range (Fig. 11.5). The slope of straight lines is

used to calculate ΔU_{dip}. An extrapolation of this straight line $K\frac{1}{T} \to 0$ $(T \to \infty)$ should give a segment equal to $\log \tau_0$.

The values of τ_0 obtained by such extrapolation are usually equal to 10^{-12}-10^{-13} s for dipole-group losses, i.e., they have a reasonable meaning of the thermal vibration time of atoms. In this case, $\Delta U_{dip.\ group} = 10$-$12$ kcal/mole. For dipole-segmental losses, the values of $\tau_0 = 10^{-30}$ s are usually obtained, and this has no physical meaning whatsoever. Therefore, the activation energy calculated

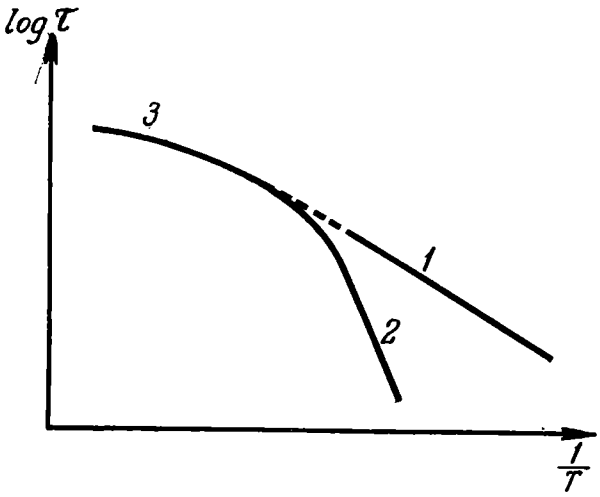


Fig. 11.5. Dependence of relaxation time on inverse temperature:
1—dipole-group losses; *2*—dipole-segmental losses

from the slopes of such straight lines that has the values of 80-140 kcal/mole is known as "apparent" activation energy.

Unreasonable values of τ_0 are observed as a result of the extrapolation of straight lines obtained in a narrow temperature range. In reality, as several authors have shown, the relationship $\tau = f\left(\frac{1}{T}\right)$ in a wider temperature range is expressed by curve *2* (Fig. 11.5), which merges with the curve of dipole-group losses in the high-temperature range. In this case $\tau_0 = 10^{-12}$ s, and the values of ΔU_{dip} depend on temperature. High values of activation energy that correspond to lower temperatures indicate the cooperation of segmental motion, i.e., motion of composite supermolecular structures, which are destroyed by thermal motion as temperature rises, and this results in reduction of ΔU_{dip}.

Many researchers use the equation of the theory of absolute rates of chemical reactions (p. 55) for calculating the activation parameters of dielectric polarization:

$$\tau = \tau_0 e^{\frac{\Delta G_{dip}}{RT}} \equiv \tau_0 e^{-\frac{\Delta S_{dip}}{R}} \cdot e^{\frac{\Delta H_{dip}}{RT}} \qquad (11.16)$$

where ΔG_{dip}, ΔH_{dip} and ΔS_{dip} = free energy, enthalpy and entropy of dielectric polarization, respectively.

Taking logarithms of Eq. (11.16), we obtain

$$\log \tau = \log \tau_0 - \frac{\Delta S_{dip}}{R} + \frac{\Delta H_{dip}}{2.303R} \cdot \frac{1}{T} \qquad (11.17)$$

It follows from Eq. (11.16) that

$$\Delta G_{dip} = 2.303RT \log \frac{\tau}{\tau_0} \qquad (11.18)$$

The magnitude of ΔG_{dip} is calculated by the value of $\tau_0 = 10^{-12}$ s, ΔH_{dip} is determined by using the graph of the $\log \tau$ vs. $1/T$ dependence, and then ΔS_{dip} is found by their difference.

11.2.2. Effect of Chemical Constitution of Polymers on Dielectric Loss

Dielectric loss in polymers — $\tan \delta_{max}$ (or ε''_{max}) — and its most probable relaxation time depend on the chemical constitution of the repeating unit in the chain. The nature and number of polar

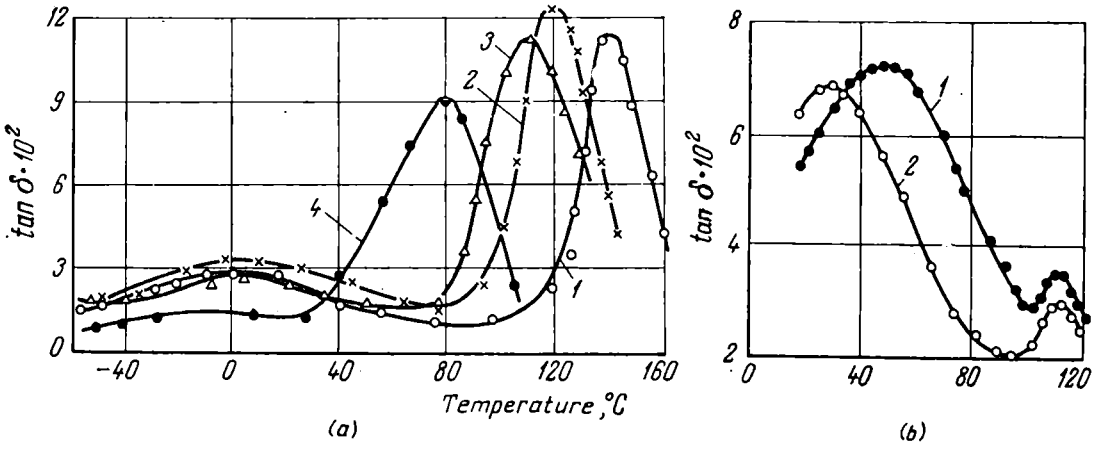


Fig. 11.6. Temperature dependence of tan δ:
(*a*) for some acetals of poly(vinyl alcohol) at 1 cps: *1*—ethylal; *2*—propylal; *3*—butyral; *4*—octylal; (*b*) for poly(methyl methacrylate) at: *1*—12.5 cps; *2*—75 cps.

groups, substituent size, side-radical isomerism, and steric and some other factors are important.

In the majority of polymers dipole-segmental loss is higher than dipole-group loss, though the reverse is true of some polymers [poly(methyl methacrylate), cellulose triacetate, etc.] (see Fig. 11.6).

Dipole-segmental loss depends on the chemical constitution of polymers, which influences intra- and intermolecular interactions,

and hence on unit mobility and relaxation time. The greater the intra- and intermolecular interactions, the less mobile are the repeating units, the higher is the temperature at which maximum tan δ occurs, and the longer is the relaxation time. Exchange of nonpolar substituents for polar ones increases intra- and intermolecular interaction; a decrease in intermolecular interaction can be achieved by introducing large hydrocarbon (alkyl) radicals into the side chain.

The effect of the size of alkyl radical on the value of tan δ was studied for poly(alkyl methacrylate), poly(vinyl acetal), poly(alkyl-α-chloracrylate), and poly(alkyl acrylate) series. In all cases, increasing the length of the alkyl radical shifted the $\tan \delta_{max}$ of the dipole-segmental loss towards lower temperatures (Fig. 11.6). At the same time the $\log f_{max}$ vs. $1/T$ dependencies also shift towards lower temperatures. This means that the relaxation time of the orientation moment decreases with decreasing concentration of polar groups in the polymer chain.

Lengthening the alkyl radical does not affect the relaxation time of the dipole-group loss, at least in the first two or three members of the poly(alkyl methacrylate) and poly(alkyl-α-chloracrylate) series. In the homologous series of poly(vinyl acetals), and poly(alkyl acrylates) and poly(vinyl acetate) the temperature, at which the $\tan \delta_{max}$ of dipole-group loss occurs, decreases with increasing homologue number.

Introduction of very bulky substituents into the side chains or increasing the branching of side chains always sharply reduces molecular mobility.

Of great importance in the case of side substituents of the same size is their polarity. Exchanging a nonpolar group for a polar one enhances intermolecular interaction and decreases the mobility of the units, increasing the relaxation time of dipole-segmental-type processes.

The curves in Fig. 11.7 are the temperature dependencies of tan δ and ε′ for poly(alkyl-α-chloracrylates) and poly(alkyl methacrylates).

Figure 11.7*a* shows that if an α-methyl group connected to the main chain is replaced by a chlorine atom, the nature of the temperature dependence of tan δ changes sharply. This is the most pronounced in the first representatives of the series.

Introduction of a chlorine atom greatly increases the $\tan \delta_{max}$ of the dipole-segmental loss, but does not change the dipole-group loss perceptibly. As a result, the tan δ in the region of maximum dipole-group loss even for the first representative of the series — poly(methyl-α-chloracrylate) — is several times smaller than the $\tan \delta_{max}$ of the dipole-segmental loss, though the reverse ratio is observed in the case of poly(methyl methacrylate).

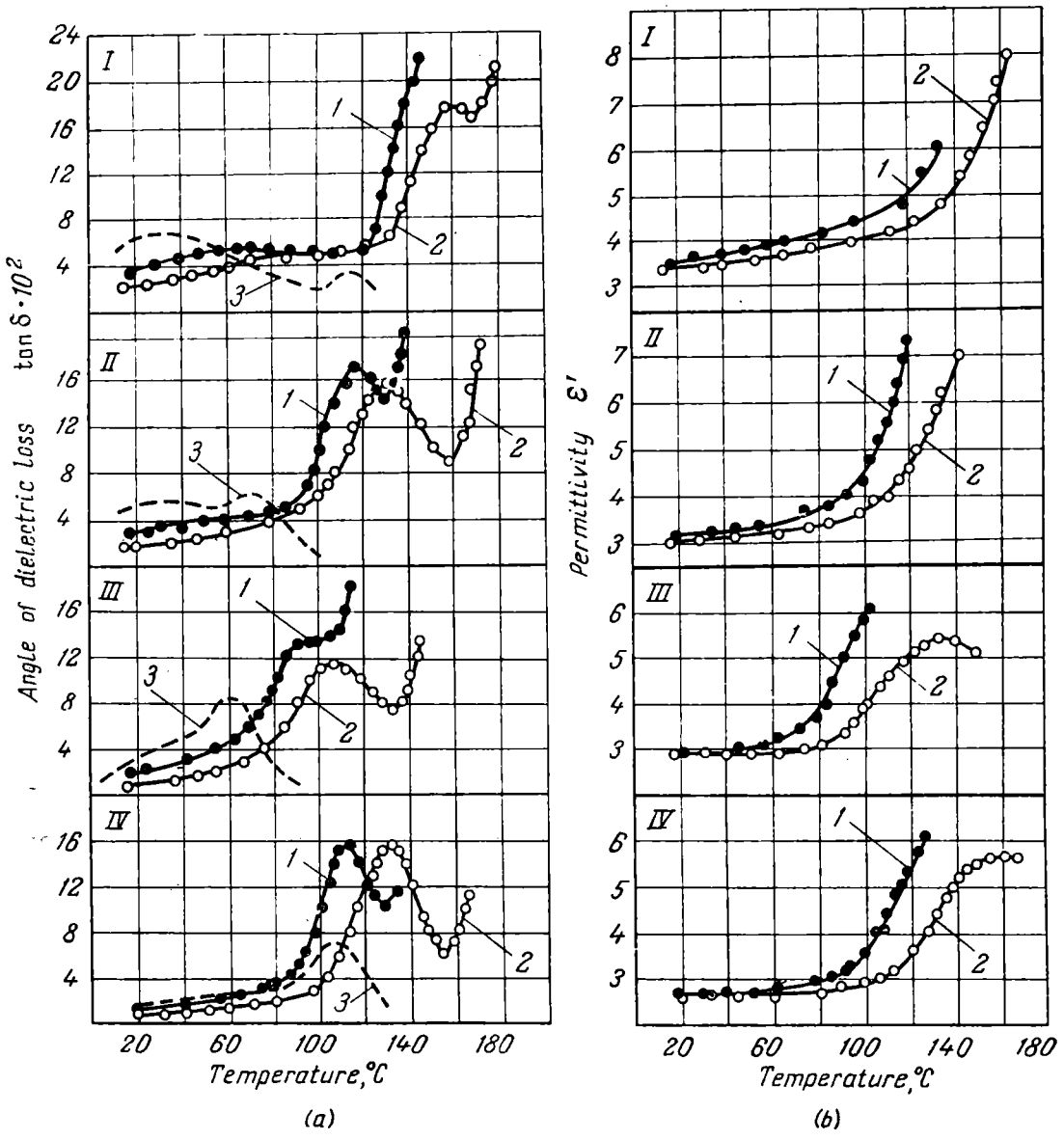


Fig. 11.7. Temperature dependence of tan δ (*a*) and ε′ (*b*) for polymeric alkyl-α-chloracrylates (*I* — methyl-α-chloracrylate; *II*—ethyl-; *III*—propyl-; *IV* — isopropyl-α-chloracrylate):

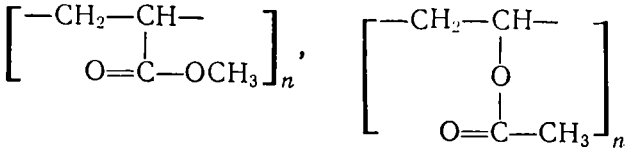
1—at 20 cps; *2*—at 400 cps; *3*—the same dependence for poly(alkyl methacrylate) at 20 cps

The relaxation times of both processes increase when a chlorine atom is introduced in the α-position, evidence of which is the shift of tan δ_{max} towards higher temperatures.

If the chlorine atom substitutes the methyl group at the end of a side chain rather than in an α-position in the main chain, two dipole-group loss maxima are observed, as has already been mentioned. Thus, the nature of the tan δ vs. *T* dependence is determin-

ed to a great extent not only by the number of polar groups, but also by their position in the macromolecular unit.

The effect of unit isomerism on the dielectric properties of a polymer has been studied for poly(methyl acrylate) and poly(vinyl acetate)



It can be seen from the formulas of these substances that they differ in the way their side chains are connected to the ester oxygen, for which reason the values of tan δ_{max} of dipole-segmental loss and of τ are higher for poly(vinyl acetate) than for poly(methyl acrylate).

The dipole-group loss characteristics of these polymers, namely their maximum tan δ and relaxation times, also differ substantially. Thus, the tan δ_{max} of dipole-group loss of poly(methyl acrylate) is almost seven times greater than that of poly(vinyl acetate), though the former maximum is 60 °C lower.

11.2.3. Dielectric Loss of Copolymers

The properties of a copolymer chain composed of different randomly alternating monomeric units depend on the constitution of the monomeric units and on their ratio. These factors also affect the dielectric properties of copolymers.

Figure 11.8 shows the temperature dependence of tan δ for copolymers of methyl acrylate (MA) and methyl methacrylate (MMA) with styrene. The only difference between these copolymers is that one of them has α-methyl groups in its molecule, which affects its properties considerably. Within the temperature interval indicated in the figure all the samples display two dipole loss regions where tan δ passes through a maximum. Dielectric losses below the T_g of the polymer should be classed as dipole-group, and those above T_g, as dipole-segmental.

It is evident from Fig. 11.8 that in both cases the dipole-group loss rises monotonically with increasing content of the polar component. A change in ratio of the components in the MA-styrene copolymer causes no shift of tan δ_{max} along the temperature axis, whereas in the case of the MMA-styrene copolymer tan δ_{max} shifts towards lower temperatures with increasing styrene content, this meaning that the relaxation time of dipole-group loss is decreasing.

Still greater differences are found in the constitution of copolymers if the dipole-segmental loss is examined. Thus, the tan δ_{max}

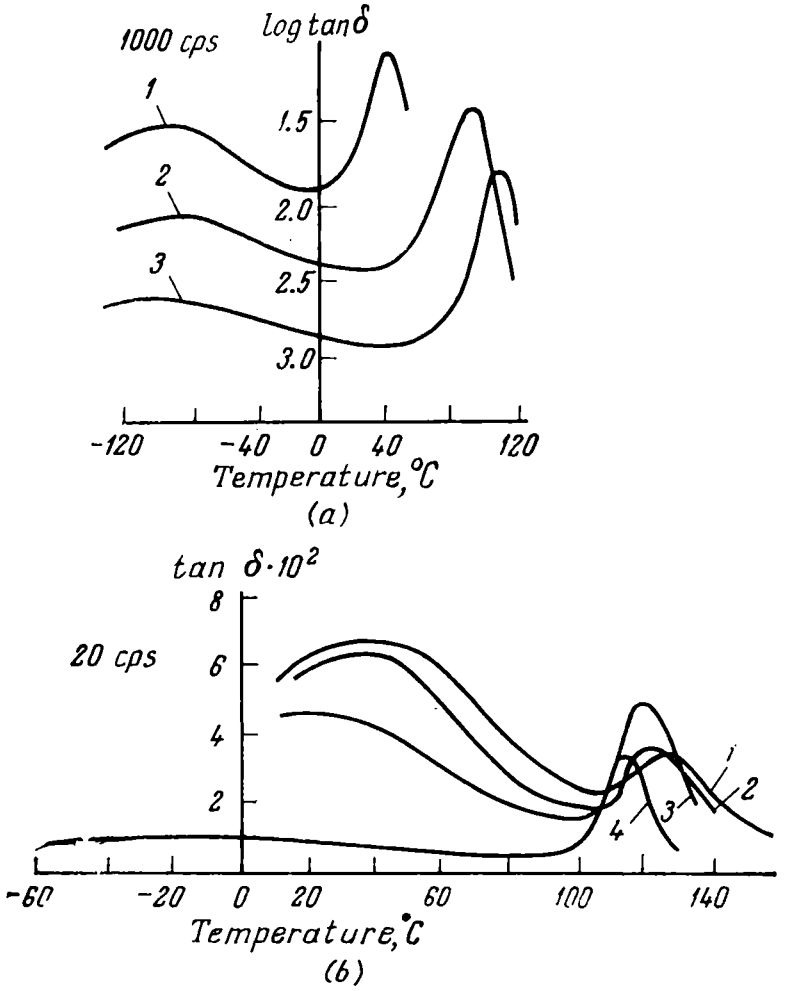


Fig. 11.8. Temperature dependence of tan δ of copolymers of methyl acrylate and methyl methacrylate with styrene:

a — MA-styrene; *1* — 100 : 0 mole per cent; *2* — 40 : 60; *3* — 14 : 86 mole per cent; *b* — MMA-styrene copolymer; *1* — 100 : 0 mole per cent; *2* — 93 : 7; *3* — 81 : 19; *4* — 24 : 76 mole per cent

of MA-styrene copolymers rises monotonically with increasing content of the polar component, whereas in the case of the MMA-styrene copolymer it varies along a curve with a maximum (Fig. 11.9). The temperature corresponding to the tan δ_{max} of the dipole-segmental loss varies monotonically with increasing content of the polar component in the MA-styrene copolymer, while in the case of the MMA-styrene copolymer it varies along a curve with a minimum.

This difference in behaviour of the copolymers is due to the simultaneous effect on the dielectric loss of two factors, namely, the polarity of the substituent and steric hindrances. α-Methyl groups always increase steric hindrances to rotation of the units (p. 107). Therefore decreasing the number of methyl groups (increasing the

styrene content) facilitates orientation of the units and increases $\tan \delta_{max}$ despite the decrease in the number of polar groups. At a styrene content of approximately 50 mole per cent the polarity

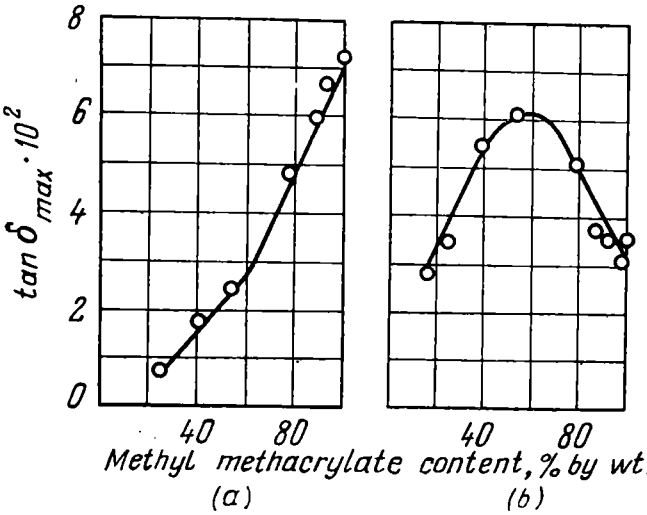


Fig. 11.9 Dependence of $\tan \delta_{max}$ on methyl methacrylate/styrene ratio of copolymers:
a — dipole-group loss at 400 cps; *b* — dipole-segmental loss at 20 cps

factor begins to manifest itself: the number of dipoles per unit volume decreases and this lowers the dielectric loss.

11.2.4. Effect of Stereoregularity on Dielectric Loss

The presence, length and quantitative ratio of syndiotactic or isotactic sections in macromolecules have a substantial effect on the mobility of segments and groups, and hence on the dielectric characteristics of a polymer.

Figure 11.10 presents the temperature dependences of the tan δ of isotactic (*1*), syndiotactic (*2*), and atactic (*3*) samples of poly(methyl methacrylate). It is evident from the figure that the temperature dependences of the tan δ of dipole loss coincide almost completely in syndiotactic and atactic poly(methyl methacrylate) over a wide temperature range. In the case of the syndiotactic sample the region of dipole-segmental losses is only shifted towards higher temperatures, which is the evidence that movement of the chain segments of the syndiotactic polymer is more restricted than in the atactic polymer, and is in accord with the higher T_g of the former. Therefore it may be thought that the relaxation times of the dipole-group process, related to the mobility of side chains, are practically the same in syndiotactic and atactic poly(methyl methacrylate).

Of an entirely different character is the temperature dependence of tan δ for isotactic poly(methyl methacrylate). While the presence of a wide dipole-group loss region, where $\tan \delta_{max}$ is more than twice as high as the corresponding value for dipole-segmental loss, is characteristic of the atactic polymer, in the case of the isotactic polymer there is a sharp "redistribution" of maximum tan δ values of the two kinds of loss. As in the case of many other vinyl polymers, the $\tan \delta_{max}$ of isotactic poly(methyl methacrylate)

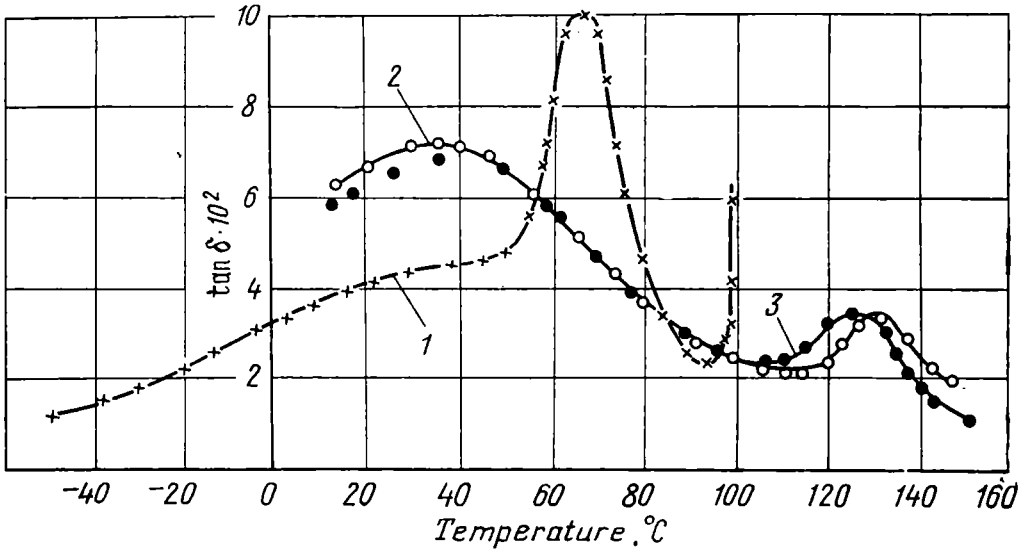


Fig. 11.10. Temperature dependence of tan δ of stereoregular poly (methyl methacrylate) samples at 20 cps:
1—isotactic; *2*—syndiotactic; *3*—atactic

is much higher for dipole-segmental than for dipole-group loss. The size of the isotactic chain sections of poly(methyl methacrylate) can be determined qualitatively from the character of its temperature-frequency dependencies of tan δ.

Stereoblock polymers display two regions of dipole-group loss $\tan \delta_{max}$, corresponding to the movements of kinetic groups in the syndiotactic and isotactic sections of the macromolecules. The position of $\tan \delta_{max}$ of one of these regions coincides with that for the fully syndiotactic polymer, and the position of the other, with the temperature-frequency coordinates of $\tan \delta_{max}$ of the fully isotactic sample.

11.2.5. Effect of Crystallization on Dielectric Loss

The regularities described in this chapter have pertained to amorphous polymers, but all that has been said is valid for crystalline polymers as well, where the picture is somewhat compli-

cated due to the difficulty of orientation of dipoles in crystalline regions.

Of substantial importance are not only the crystallinity of polymer but also the size, defects and type of crystalline formations. With increasing crystallinity of a polymer its conductivity decreases and its breakdown voltage rises. If the crystallinity of a polymer is high, it may not display dipole-segmental losses, which are associated with the movements of the macromolecular segments in its amorphous parts (such is the case with polyethylene). There may appear a relaxation region of dipole losses due to movement of chains inside the crystalline formations, e.g., inside lamellae. (In the literature this relaxation process is often denoted by α_c.)

Each crystalline modification has its own characteristic $\tan \delta_{max}$ or ε''_{max} values and its own relaxation times of the α_c region. At lower temperatures dipole losses are observed, which are related to movement of polar groups or short macromolecular sections in the amorphous regions or near the boundaries of the crystalline formation. The corresponding processes are often denoted by γ_I, γ_{II}, etc.

11.2.6. Other Factors Affecting Dielectric Loss

The appearance of dipole-segmental and dipole-group losses in polymers is associated with the mobility of the kinetic units of the macromolecular chain. For this reason factors determining molecular mobility affect dielectric loss in polymers. These include orientation of polymeric chains and packets, chain crosslinking, pressure, and the influence of low-molecular admixtures, particularly plasticizers.

Experiment shows that extension of a polymer may increase or decrease the relaxation time of its dipole-segmental loss depending on whether extension results in compacting or loosening of the molecular packing (Chap. 10).

Crosslinking of macromolecules always decreases segment mobility and increases the relaxation time of dipole-segmental loss. The temperature dependence of $\tan \delta_{max}$ of dipole-segmental losses is determined by the length of the crosslinks and the distance between them (network chain length). By way of example we may mention the shift of the $\tan \delta_{max}$ of dipole-segmental loss towards higher temperatures, caused by increasing the degree of vulcanization of natural rubber, or of crosslinking of epoxy resins.

Pressure influences the relaxation times of processes in which intermolecular interactions play an important part. Thus, raising the pressure increases the relaxation time of dipole-segmental loss

considerably and that of dipole-group loss to a lesser degree. The effect of plasticizers on dielectric loss in polymers will be discussed in Chap. 16.

11.2.7. Dielectric Polarization and Dipole Moments

Dipole Moments of Low-Molecular Substances. By studying the dielectric polarization of a substance one can determine the dipole moment μ_0 of its molecules, related to its permittivity or dielectric constant ε by Eq. (11.8) (p. 309). The value of the dipole moment gives grounds for certain conclusions as to the charge symmetry in the molecule, the presence of isomerism, and the arrangement of radicals in complex organic compounds, i.e., enables characterization of the stereochemical structure of the molecule. Dipole moments are usually determined in the gas phase or in a solution of the polar substance in a nonpolar solvent, where with infinite dilution the interaction of the polar molecules with each other can be neglected. For a solution Eq. (11.8) can be written as follows:

$$\frac{\varepsilon-1}{\varepsilon+2}\cdot\frac{1}{d}(M_1N_1+M_2N_2)=\frac{4}{3}\pi N_A\left(N_1\alpha_1+N_2\alpha_2+N_2\frac{\mu_0^2}{3kT}\right) \quad (11.19)$$

where M = molecular mass
N_i = mole fraction
N_A = Avogadro's number
α = polarizability.

Equation (11.19) can be written in a more general form:

$$P_{1,2}=N_1P_1+N_2P_2 \quad (11.20)$$

where $P_{1,2}$, P_1, and P_2 are the polarizations of solution, solvent and solute.

In practice one determines (by measuring the dielectric constant) the polarization of the solution depending on the concentration of solute and extrapolates to zero concentration, i.e., obtains the polarization of the polar substance at infinite dilution $P_{2\infty}$. Then the dipole moment is calculated from the formula

$$\mu_0=\sqrt{\frac{P_{2\infty}-P_1}{4\pi N_A}\cdot 9kT} \quad (11.21)$$

Since Eq. (11.8) and hence Eqs. (11.19) and (11.21) are applicable only to polar gases and solutions of polar substances in nonpolar solvents, a more rigorous equation derived on the basis of the statistical theory of polarization, which takes into account long-range interaction (see p. 95) should be employed when investigating polar liquids and other systems in which molecular

interaction occurs. In this case the following equation is recommended:

$$(\varepsilon - n^2) = \frac{4\pi N_A}{V} \cdot \frac{\varepsilon}{2\varepsilon + n^2} \left(\frac{n^2 + 2}{3}\right)^2 \frac{\mu_{eff}^2}{kT} \qquad (11.22)$$

where ε = dielectric constant of medium
n = refractive index
V = molar volume
N_A = Avogadro's number
μ_{eff} = effective dipole moment.

The quantity μ_{eff} in Eq. (11.22) differs from μ_0 in Eq. (11.19). The difference is due to the fact that dipole moments in systems involving intermolecular interaction are not equal to dipole moments of isolated molecules, owing to interaction between closest neighbours.

The general relation between μ_0 and μ_{eff} can be written as

$$\mu_{eff}^2 = \mu_0^2 g \qquad (11.23)$$

where g is a correlation parameter taking into account short-range intermolecular interaction.

The parameter g depends on the energy of intermolecular interaction and on the number of closest molecules.

The statistical theory of polarization derives the following relation between these two quantities:

$$g = 1 + Z \overline{\cos \gamma} \qquad (11.24)$$

where Z = number of closest molecules
$\overline{\cos \gamma}$ = average cosine of the angle between them, its value depending on the energy of interaction between neighbouring molecules ΔU and the mutual orientation of the molecules dr:

$$\overline{\cos \gamma} = \frac{\int \cos \gamma e^{-\Delta U/kT} \, dr}{\int e^{-\Delta U/kT} \, dr}$$

Thus, the correlation parameter g characterizes retarded rotation of neighbouring molecules due to interaction between them.

The value of g is found from Eq. (11.23) by comparing the values of the effective dipole moment μ_{eff} measured in a condensed system (e.g., in a polar liquid) with those of the dipole moment in a solution where there is no intermolecular interaction of polar molecules; μ_0 is determined from Eq. (11.19).

In some cases the mutual orientation of dipoles of neighbouring molecules can be deduced from the value of the correlation parameter. If a molecular arrangement is possible in the liquid, whereby their dipole moments are antiparallel, the value of g is less than unity; if the arrangement is parallel, g is greater than unity. It should be pointed out that the greatest deviation of the correlation parameter from unity is observed in compounds with hydrogen bonds. The experimental values of the correlation parameter for some compounds at 20 °C are given below:

Methyl alcohol	3.0	Butyl alcohol	3.3
Ethyl alcohol	3.1	Butyl bromide	0.76
Propyl alcohol	3.1	Butyl chloride	0.85

It follows from the above data that alcohols are characterized by high positive values of their correlation parameters, due to the presence in them of hydrogen bonds, which causes parallel orientation of their polar groups. The correlation parameter of the last

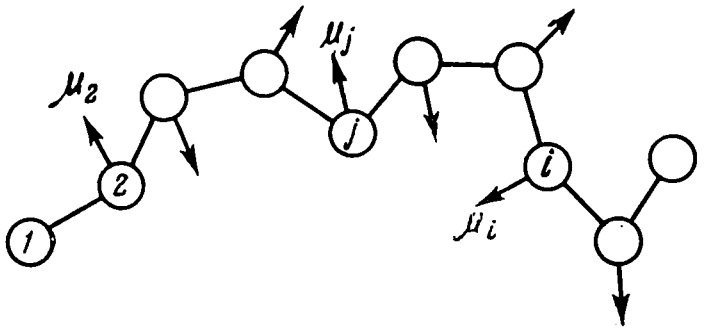


Fig. 11.11. Orientation of dipole moments of polar units in a polymer molecule

two compounds is less than unity, which is evidence of antiparallel arrangement of the polar groups in butyl bromide and chloride, partially compensating for their dipole moments.

Thus, investigation of dielectric polarization and dipole moments yields data for studying intermolecular interaction.

Dipole Moments of Macromolecules. The dipole moment of a polymer macromolecule depends not only on the stereochemical constitution of its monomeric unit, but also on chain conformation. Figure 11.11 is a diagram of dipole orientation in a polymeric molecule. Each chain conformation is characterized by a dipole moment equal to the vectorial sum of dipole moments of the polar groups distributed along the chain. For this reason, the dipole moment of the whole macromolecule depends primarily on the conformational properties of the polymeric chain. If the chain conformation is very rigid, as may be the case in rod-like and helical structures, the macromolecule should orient itself in an electric

field as an integral whole. The total dipole moment of such a macromolecule is found from the relation

$$M^2 = N^2\mu_0^2 \tag{11.25}$$

where M = dipole moment of entire macromolecule
μ_0 = dipole moment of monomeric unit
N = number of units in the chain.

In polymers of such rigid structure with molecular masses of 10^5-10^6, anomalously high dipole moments should be expected compared to low-molecular substances. Experimental proof of this assumption was obtained in a study of the dipole moments of synthetic polypeptides, and recently, of polyisocyanates. The dipole moments of polymers of such structure amount to 10^3 Debye units (D). The total macromolecular dipole moments of flexible polymeric coils are of the order of tens of debyes at the same molecular masses. This is due to the fact that in the case of real coiled polymeric chains without a rigid secondary structure individual chain units orient themselves in an electric field. As shown by Kuhn, for flexible coils with freely jointed monomeric units

$$\overline{M}^2 = N\mu_0^2 \tag{11.26}$$

The orientation of polar monomeric units in real polymeric chains is determined by the hindrance to internal rotation in the chain, and the dipole moment of the entire macromolecule can be found from

$$\overline{M}^2 = N\mu_{\text{eff}}^2 = N/\mu_0^2 g \tag{11.27}$$

The effective dipole moment (μ_{eff}) of a monomeric unit of the polymeric chain is, in the general form, a function of the parameters characterizing the hindrance to internal rotation in the polymeric chain. A relative measure of hindrance to internal rotation is the quantity g, i.e., the correlation parameter,

$$g = \mu_{\text{eff}}^2/\mu_0^2 \tag{11.28}$$

Thus, unlike low-molecular compounds, in which an isolated molecule is characterized by the value of its dipole moment μ_0, the dipole moment referred to one unit in a polymeric chain is characterized by its effective value, which depends not only on the repeating unit structure, but also on intramolecular interaction. For this reason at present when studying dipole moments of polymers one starts by examining intramolecular interaction.

Of special interest is the study of dipole moments of polymers in dilute solutions, where there is no interaction between neighbouring polymer molecules. In this case the dipole moment should be calculated by means of Eq. (11.22), modified for an infinitely

dilute solution, which gives the value of the effective dipole moment μ_{eff} per polymer chain unit. If, besides, the dipole moment of the polymer chain unit μ_0 is known, one can determine the correlation parameter g characterizing the hindrance to rotation of the polymer chain units due to interaction between them.

The effect of hindrance to internal rotation on the dipole moment was detected in a study of polymers of different structures. Table 11.2 gives the effective dipole moments per monomeric unit of several polymers, the dipole moments of the corresponding low-molecular compounds and the correlation parameters g.

BLE 11.2. *Dipole Moments and Correlation Parameters of Polymers*

Compound	t, °C	Solvent	Dipole moment, D	g
Poly(vinyl acetate)	20	Benzene	1.66	0.82
Ethyl acetate	20	Benzene	1.83	
Poly(vinylisobutyl ether)	25	Benzene	1.07	0.77
Isobutyl ether	25	Benzene	1.22	
Poly*para*chlorostyrene	20	Paraxylene	1.41	0.71
*para*Chloroethylbenzene	20	Paraxylene	1.67	
Poly(vinyl chloride)	35	Dioxan	1.73	0.68
Butylchloride	35	Dioxan	2.10	
Poly(methyl methacrylate)	20	Toluene	1.33	0.61
Methyl isobutyrate	20	Toluene	1.70	

It is evident from Table 11.2 that the dipole moment of the low-molecular compound is higher than the effective dipole moment of monomer unit in the polymer chain, which gives values of $g < 1$. A value of $g < 1$ characterizes a definite correlation in the orientation of polar groups, due to intramolecular interaction in polymers.

On the basis of a large number of experimental studies of dipole moments it has been possible to estimate the hindrance to internal rotation in polymers of different monomeric unit structure and of different chain structure. The high sensitivity of dipole moment to short-range interaction also becomes evident when studying stereoregular polymers. Polymers of iso- and syndiostructure have different conditions of internal rotation, giving different values of their effective dipole moments and g. Thus, for poly(*tert*-butyl methacrylate) of isotactic structure $\mu_{eff} = 1.73$ D, whereas that of atactic structure has $\mu_{eff} = 1.54$ D.

Of great interest is the study of the dipole moments of random copolymers of a polar monomer with a nonpolar one. Investigation

of various random copolymers showed that their effective dipole moments vary with varying content of the polar monomer. Figure 11.12 shows the change in effective dipole moment depending on composition for methyl methacrylate-styrene copolymers. It is evident from the figure that the effective dipole moment calculated per polar monomeric unit in the copolymer depends on the composition of copolymer, increasing with decreasing polar monomer

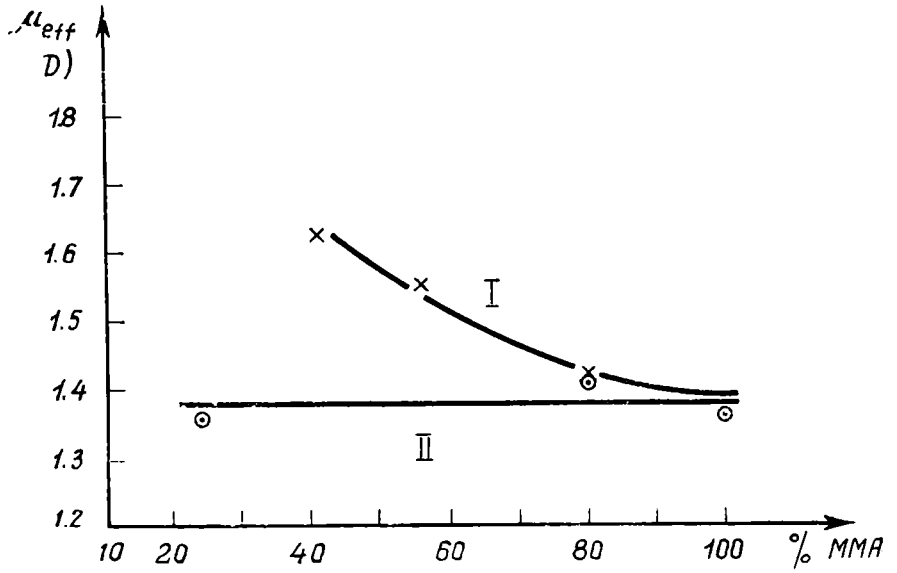


Fig. 11.12. Effective dipole moments versus composition for methyl methacrylate-styrene copolymers:
I—random copolymers; *II*—block copolymers

content. This reflects the change in the conditions of internal rotation and the weakening of interaction of polar groups when they are separated by nonpolar units. At the same time, as distinct from random copolymers, the dipole moment of a block copolymer is independent of composition and remains equal to the dipole moment of the homopolymer. This allows us when studying copolymers by the dipole moment method to get information showing whether the chain units alternate at random or the chain has block-type microstructure.

Besides determination in solution, dipole moments are at present calculated by formula (11.22) for polymers above their glass-transition temperatures. The possibility of such an estimate depends on the availability of polarization theories that take into account intermolecular interaction. This makes it possible to obtain certain information on intermolecular interaction in polymers by comparing correlation parameter values in solution and in the rubber-like state. Table 11.3 gives the correlation parameters of some polymers in solution and in the rubber-like state. Although

TABLE 11.3. *Correlation Parameters of Some Polymers in Solution and in the Rubber-Like State*

Polymer	g	
	In solution	in the rubber-like state
Poly(methyl methacrylate)	0.61	0.7
Poly(vinyl acetate)	0.82	0.8
Poly(methyl acrylate)	0.79	0.7

the accuracy of determination of dipole moments, and accordingly the correlation parameters, in solution is much higher than in the rubber-like state, the approximate equality of the correlation parameters in solution and at temperatures above the glass-transition temperature is an indication of the determinative effect of intramolecular interaction in macromolecules on the rubber-like behaviour of polymers.

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CHAPTER 12

Polymer-Low-Molecular Liquid Systems

The interaction of polymers with low-molecular liquids, resulting in swelling and dissolving of the polymers, is of great practical importance both for processing polymers and during service of articles made from them. For example, many synthetic fibres and films are produced from solutions. The process of plasticizing, used in the fabrication of articles from polymeric materials, is based on swelling of polymers in plasticizers. Lacquers and adhesives are polymer solutions. In all the cases mentioned it is very important for the polymers to swell and dissolve well in low-molecular liquids.

On the other hand, during service articles made of polymeric materials very often come into contact with various liquid media (gasoline, oil, water, etc.) and it is very important for the articles not to interact with these media. Obviously, to solve the question as to which liquid a given polymer dissolves in and to which liquid it is resistant, it is necessary to have a good knowledge of the regularities of interaction of polymers with low-molecular liquids, i.e., of the theory of solutions of macromolecular compounds.

Polymer-low-molecular liquid systems may be classified into true solutions, colloidal dispersions and gels.

12.1. TRUE SOLUTIONS OF POLYMERS

12.1.1. Specific Properties of True Solutions

A true solution is a multicomponent system which has the following characteristic features:

(1) affinity * between components,

* For details on affinity, see Chap 13.

(2) spontaneous formation,
(3) constant concentration in time,
(4) homogeneity, i.e., presence of only one phase,
(5) thermodynamic stability.

Let us examine these features in detail. True solutions can form when there is affinity, i.e., interaction between the components. If this is the case, the components disperse spontaneously, when they come in direct contact, into molecules, atoms, or ions without the expenditure of external work. Such spontaneous dispersion is called *dissolution* or mutual *mixing* of the components, which are capable of being dispersed, i.e., crushed to molecules or ions. Therefore, true solutions are said to be characterized by a molecular degree of dispersion. However, apart from molecules, true solutions may contain their aggregates, or "clusters", which consist of several molecules. These clusters are continually destroyed by thermal motion and then reoriginate due to intermolecular interaction. Such formations are known as *fluctuation* formations. They may be *associates*, i.e., aggregates of homogeneous molecules, or *solvates*, i.e., aggregates of heterogeneous molecules. The formation of fluctuation structures which are recoverably destroyed in solutions is known as *association* or *solvation*, respectively.

Components may mix in any proportion (*complete miscibility*) or in definite proportions (*partial miscibility*). Mixing results in a solution of a definite composition, i.e., a definite concentration. If the external conditions (pressure, temperature) do not vary, the concentration of a true solution remains constant in time.

A true solution is a *one-phase system* *.

The solution phase may be separated from other phases (precipitate, vapour, or solution) by an interface, but within the solution itself there is no interface, i.e., the system is homogeneous.

The most important feature of a true solution is its *thermodynamic stability* or equilibrium state. A system is called thermodynamically stable if its formation is accompanied by a decrease in the Helmholtz free energy (at constant volume and temperature) or by a decrease in the Gibbs free energy G (at constant pressure and temperature). The Gibbs free energy decreases to a definite equilibrium value which does not change subsequently with time.

If we denote the Gibbs free energy of 1 mole of solution by G_{sol}, and that of 1 mole of the components before mixing by $\sum G_{comp}$, then $G_{so} < \sum G_{comp}$ or $\Delta G < 0$ At equilibrium $G_{sol} = \sum G_{comp}$ and $\Delta G = 0$ (this will be discussed in greater detail in Chap. 13).

A system whose Gibbs free energy does not vary is called an *equilibrium system*, a true state of equilibrium being characterized

* The definition of phase is given on. p. 147.

by that it is independent of the path of the process. For instance, at definite pressure and temperature a two-component true solution has definite composition and properties independent of whether the solution was prepared from a colder solution by heating or from a hotter one by cooling.

12.1.2. Dissolution and Swelling of Polymers

Like low-molecular substances, a polymer cannot dissolve in all liquids. In some liquids, which are *good* * solvents for a given polymer, it dissolves spontaneously (on direct contact with them). A polymer does not undergo any changes on contact with other liquids (*poor solvents* or *nonsolvents*). For example, natural rubber dissolves spontaneously in benzene, but will not interact with water. Gelatin dissolves well in water, but will not interact with ethyl alcohol. Obviously, in some cases the polymer and the low-molecular liquid possess mutual affinity, while in others no such affinity exists. In the former case the formation of a true solution may be expected, but in the latter case only a colloidal solution can form. Indeed, spontaneously forming solutions of polymers have all the features of true solutions, including the main feature—reversibility and equilibrium, which is evidenced by investigations of the applicability of the phase rule to polymer solutions (p. 348). However, true solutions of polymers have their specific features, which distinguish them from true solutions of low-molecular substances. These include swelling prior to dissolving, high viscosity, slow diffusion, and inability to pass through semipermeable membranes. All these features are due to the great difference in size between the particles of the components mixed.

Spontaneous solution of polymers is often observed in practice, but this process has a characteristic feature: before dissolving the polymer "swells", i.e., absorbs the low-molecular liquid, increasing in mass and volume. If a polymer sample is cut up into small pieces and a solvent is poured over them, each piece will swell separately at first, but afterwards they will all merge to form a uniform liquid layer consisting of the polymer and the liquid it has absorbed. At this juncture the system is a true solution of the liquid in the polymer, the latter playing the part of the solvent and the former, of the solute. Swelling is not merely the penetration of small solvent molecules into the polymer phase, involving filling of the cavities or pores of the latter, as in the sorption of liquids or vapours by porous solid sorbents. Swelling inevitably involves a change in polymer structure, which sharply increases the volume of the sample. Swelling may be limited or unlimited.

* For good and poor solvents, see Chap. 13.

Unlimited swelling is swelling that passes spontaneously into dissolution. It is analogous to complete miscibility of liquids, such as water and ethyl alcohol or water and sulphuric acid. If one liquid is poured carefully onto a layer of the other, they penetrate into each other; with water and ethyl alcohol, molecules of the latter pass into the water phase, and water molecules, into the alcohol phase. Since the molecules of both liquids are small and mobile, they penetrate into each other at equal rates and the liquids mix.

The specific feature of dissolving of a polymer is that the molecules of the mixing components differ in size by thousands of times and hence have different mobilities. The mobility of the molecules of a low-molecular liquid is very high and that of macromolecules is very inconsiderable. Therefore, large macromolecules do not have time to pass over to a solvent phase: before dissolving, a polymer absorbs a large amount of liquid, i.e., it swells.

Swelling is *one-directional mixing* due to the large size of the polymer molecules. This is supported by the fact that degraded polymers dissolve without preliminary swelling.

The swollen polymer, which is a solution of a low-molecular liquid in the polymer, coexists for some time with the layer of pure low-molecular liquid. After some time, when the polymer chains have moved apart to a sufficient extent, they begin to diffuse slowly into the solvent. There appears a layer of a more dilute solution, coexisting with the layer of more concentrated solution. After some more time has passed the concentrations of these two layers become equal and they merge into a one-phase homogeneous system.

Limited swelling is the interaction of polymers with low-molecular liquids, when it is limited to the stage of sorption of the latter by polymer; spontaneous solution of the polymer does not occur, i.e., the polymer chains do not separate completely from one another. As a result, two coexisting phases are formed, one of them being a solution of low-molecular liquid in polymer, and the other, the pure low-molecular liquid (if the polymer is incompletely insoluble) or a dilute solution of polymer in low-molecular liquid. These phases are separated by a clearly visible interface, and are in equilibrium.

Distinction should be made between limited swelling of linear and of crosslinked polymers. In the case of linear polymers the process is analogous to partial mixing of liquids: under definite conditions (temperature, concentration of components) swelling is limited, but if the conditions are changed appropriately, unlimited solution may ensue.

Limited swelling of linear polymers may be accounted for by the fact that the energy of interaction of chains with one another

is higher than the energy of their interaction with the solvent molecules, so that the chains do not separate completely. Raising the temperature favours disturbance of the bonds between chain molecules, and limited swelling becomes unlimited. An example is the swelling of gelatin in water. Gelatin protein molecules have strong bonds between them, and interaction with water cannot break down these bonds completely at room temperature; therefore the gelatin swells to a limited extent. Only if heated to 35-40 °C does a homogeneous solution form.

If the polymer has a spatial network composed of chemical bonds, the chains cannot be separated at any temperature (below the decomposition temperature of the polymer). Hence, crosslinked polymers are inherently insoluble, but they may swell, forming gels (p. 358).

Swelling is a process of sorption of a low-molecular liquid by a polymer, being accompanied with a change in polymer structure. Penetrating into interstructural space, solvent molecules cause supermolecular structures of polymers to pry apart (*interstructural swelling*). If they penetrate into structures, macromolecules are pried apart (*intrastructural swelling*). As the solvent content increases, the polymer structure gradually disintegrates, and a fluctuation polymer network (p. 531) containing a solvent is formed in a solution. On further dilution, the network disintegrates into aggregates or associates of macromolecules, and then, in very dilute solutions, into separate macromolecules.

A solution passes over from a dilute stage to a more concentrated one reversely: associates of macromolecules are formed, and then a fluctuation network originates. Associates in polymer solutions have a longer lifetime than associates in the solutions of low-molecular substances, but they are recoverably destroyed by thermal motion, i.e., they have a fluctuation nature, like a network.

12.1.3. Degree and Kinetics of Swelling

From a practical point of view it is very important to know the capacity of crosslinked polymers for swelling in various liquids and vapour media. This capacity is assessed by the *degree* or *amount of swelling*, expressed as the amount of liquid (or its vapour) sorbed by unit mass or volume of the polymer.

Degree of swelling can be determined by the gravimetric or volumetric methods. The former consists in weighing the sample before and after swelling and calculating the amount of swelling α from the formula

$$\alpha = \frac{m - m_0}{m_0} \qquad (12.1)$$

where m_0 = mass of initial polymer sample
m = mass of swollen polymer sample.

The volumetric method is based on measuring the volume of polymer before and after swelling:

$$\alpha = \frac{V - V_0}{V_0} \tag{12.2}$$

where V_0 = volume of unswollen polymer
V = volume of swollen polymer.

Degree of swelling can be determined only for polymers with limited swelling, because upon unlimited swelling the polymer itself begins to dissolve and the mass of the sample decreases. The degree of swelling changes with time. The dependence $\alpha = f(t)$ is usually represented by a curve of the shape typified by Fig. 12.1. It can be seen from the figure that after a certain time the amount of swelling becomes constant. The degree of swelling corresponding to the beginning of the horizontal section of the curve is called the *maximum* or *equilibrium degree of swelling*. Different polymers take different periods of time to reach their equilibrium degree of swelling and this is of great importance. Thus, in Fig. 12.1 the maximum degree of swelling of sample *2* is higher than that of sample *1*, and hence if they are kept in the liquid in question for a long time, the second sample will swell much more than the first one. If the degree of swelling is determined after some shorter time interval, the reverse may be observed: the amount of swelling of the first sample may be higher than that of the second. Hence, the tendency of a polymer to swell should be assessed by its maximum degree of swelling.

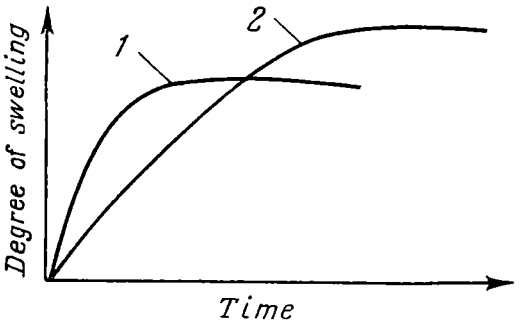


Fig. 12.1. Kinetics of swelling:
1—quick-swelling sample; *2*—slow-swelling sample

Polymers may absorb low-molecular substances not only from the liquid, but also from the gaseous phase; if the polymer swells in a liquid, it will swell in its vapours as well. The rate of swelling in vapours is much lower, but the maximum or equilibrium degree of swelling is the same.

Sometimes a phenomenon called *negative swelling* is observed in polymers, involving decrease rather than increase of sample mass in time. This occurs when polymers of linear or crosslinked structure swell owing to washing out of soluble impurities from them.

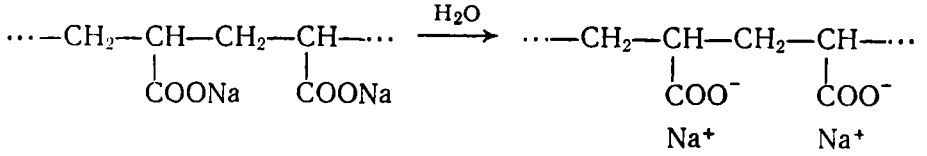
Determination of the degree of swelling is used in practice for testing finished polymer articles intended for service in liquid and gaseous media. Such determinations serve as a method of assessing the degree of crosslinking of polymer chains (p. 438).

12.1.4. Polyelectrolytic Solutions

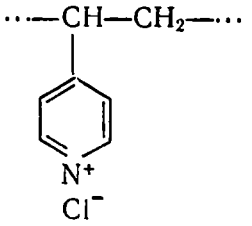
Solutions of macromolecular compounds, like those of low-molecular substances, fall into nonelectrolyte and electrolyte solutions.

Polymers which do not dissociate into ions form solutions of *polymeric nonelectrolytes*. Polymers which undergo electrolytic dissociation when dissolved form solutions of *polymeric electrolytes*. Polymeric hydrocarbons, alcohols, and halogen derivatives form nonelectrolyte solutions.

Synthetic polyelectrolytes have been obtained at present. These are polymers containing a large number of periodically repeating charges in each macromolecule and capable of dissociating in solution into ions. Examples of *polyacids* are poly(acrylic acid) and poly(methacrylic acid). The water-soluble salts of these acids dissociate in solution:



An example of *polybases* is polyvinylpyridinium:



Of great importance are so-called *crosslinked polyelectrolytes* prepared by introducing ionizing groups into various crosslinked polymers. Thus, a crosslinked polymer can be obtained by copolymerizing polystyrene with small amounts of divinylbenzene; it is then sulphonated to introduce a large number of sulphonic acid groups SO_3H. This sulphonated crosslinked polymer is insoluble in water; it only swells in it, and its sulphonic acid groups dissociate according to the equation

$$-SO_3H \longrightarrow -SO_3^- + H^+$$

The hydrogen ions eliminated can replace other ions in a low-molecular liquid. This is the basis of the action of ion-exchange resins, which are crosslinked polyelectrolytes (Chap. 21).

12.1.5. Factors Affecting Dissolution and Swelling of Polymers

One of the most complicated questions of physical chemistry is that of the causes of the mutual solubility of substances. Many generations of scientists have tried to reveal the intricate processes which occur on dissolution, and various theories of solutions were proposed. But even at present it is very difficult to explain why some substances spontaneously mix together while others do not, and, the more so, to predict such a process.

The ability of polymers to dissolve or swell is determined by many factors:

(1) chemical nature of a polymer and of a solvent;
(2) molecular mass of a polymer;
(3) flexibility of a polymer chain;
(4) packing density of macromolecules;
(5) phase state;
(6) inhomogeneity of the chemical composition of a chain;
(7) presence and density of a spatial network;
(8) temperature.

Nature of a Polymer and of a Solvent. The mutual solubility of substances depends on their chemical composition. It has long been assumed that "like dissolves like", i.e., substances similar by their chemical composition dissolve in one another, and substances which greatly differ in this respect do not. The similarity of energies of intermolecular interaction was later taken as a criterion of "likeness".

A simpler case are solutions exhibiting only van der Waals interactions, i.e., dispersion, strain and dipole-dipole interactions (p. 94). If liquids are nonpolar, i.e., if they possess a zero dipole moment and only dispersion forces operate between them, they usually mix well in a wide temperature range. According to this viewpoint, amorphous nonpolar polymeric hydrocarbons (polyisobutylene, polyisoprene, polybutadiene, etc.) can be expected to dissolve well in saturated low-molecular hydrocarbons and in their mixture (benzene), and this is observed. Such polymers do not dissolve and swell in polar liquids (acetone, etc.) and especially in liquids capable of forming hydrogen bonds (water, lower alcohols). Conversely, polymers containing polar groups (cellulose nitrate, polyacrylonitrile, etc.) do not dissolve in nonpolar liquids and tend to react with liquids of similar polarity.

The polarity of a substance is usually characterized by a value of the constant dipole moment, which, however, is not an effective measure of polarity. For example, all the aliphatic alcohols or all the ketones possess practically the same dipole moment and quite different solvent action with respect to other liquids and polymers,

which depends on the length of an alkyl radical. At the same value of the dipole moment, the longer is an alkyl radical in a molecule of alcohol or ketone, the better do nonpolar polymers, and the worse do polar polymers, dissolve or swell in them.

As a measure of intermolecular interaction, use is often made of Hildebrand's solubility parameter δ (p. 422), which is connected with the cohesion energy density (CED) of a liquid by the simple

TABLE 12.1 *Parameters of Solubility δ of Some Low-Molecular Liquids and Polymers*

Name	δ $(cal/cm^3)^{0.5}$
Low-molecular liquids	
n-Hexane	7.30
Diethyl ether	7.40
n-Octane	7.55
Carbon tetrachloride	8.60
n-Propyl benzene	8.65
Ethyl acetate	9.10
Benzene	9.15
Chloroform	9.30
Methyl ethyl ketone	9.30
1,2-Dichloroethane	9.80
Tetrahydrofuran	9.90
Acetone	10.00
n-Hexanol	10.00
Tetrachloroethane	10.40
Dimethyl acetamide	11.10
Dimethyl formamide	12.10
Ethanol	12.70
Methanol	14.50
Water	23.20
Polymers	
Silicone rubber	7.30
Polyisobutylene	7.90
Polyethylene	7.94
Polypropylene	8.10
Poly-*n*-butyl methacrylate	8.80
Polystyrene	9.10
Polymethyl methacrylate	9.30
Polyvinyl chloride	9.55
Polyethylene terephthalate	10.10
Polyarylate of phenolphthalein and of terephthalic acid	10.70
Polyimide of aniline phthalein and of pyromellitic acid	11.70

relation $\delta = \left(\frac{\Delta E_i^0}{V_i}\right)^{1/2}$, where ΔE_i^0 is the liquid evaporation energy, and V_i its molar volume. The best solvent of a given polymer is a liquid whose CED is similar to that of the polymer. This consideration is the basis of the method of determining the CED of a polymer. It consists in the measurement of the degree of swelling of crosslinked polymers in liquids having different CED and in the plotting of the graph by relation $\alpha = f(\text{CED}_{\text{liq}})$. This relation often has an extremum nature, and the CED of a liquid which corresponds to the maximum on a curve is taken as being equal to the CED of a polymer. There are also methods of calculating these parameters, and they have been used to calculate the values of δ of several polymers. Table 12.1 gives the values of δ for some liquids used as solvents and those for several polymers. The low values of δ are characteristic of nonpolar substances, while high ones are characteristic of substances which have very great dipole moments or are capable of forming hydrogen bonds.

These data are of certain interest. For example, they can be used as a basis for ascertaining that polymers with $\delta \cong 7\text{-}8$ will not dissolve in liquids with $\delta = 12\text{-}14$, while polymers with $\delta = 10\text{-}12$ will not dissolve in liquids with $\delta = 6\text{-}8$. For them, solvents should be sought for among liquids having an intermediate value of δ. But it should by no means be concluded that a given polymer dissolves in all liquids whose CED is similar to that of the polymer.

TABLE 12.2. *Donor Numbers, Dielectric Constant and Dipole Moment of Some Solvents*

Solvent	$D \cdot r$ ($SbCl_5$)	ε	μ_0	δ
Nitrobenzene	4.4	34.8	4.3	10.0
Benzonitrile	11.9	25.2	4.4	8.4
Acetone	17.0	20.7	2.9	10.0
Ethyl acetate	17.1	6.0	1.8	9.1
Water	18.0	81.0	1.8	23.5
Tetrahydrofuran	20.0	7.6	0	9.9
Dimethyl formamide	26.6	36.1	2.0	12.1
N,N-dimethyl acetamide	27.8	38.9	2.0	10.8
Dimethyl sulphoxide	29.8	45.0	4.0	12.9
N,N-diethyl acetamide	32.2	—	2.0	9.9

This is clearly seen in Table 12.2. Consequently, the value of δ of a polymer and of a solvent can far from always be used for prediction. This is clear: CED is an integral characteristic of intermolecular interaction, while the solvent action, or miscibility, of com-

ponents depends on the presence of specific functional groups between which the so-called "specific" interactions are exhibited. They include hydrogen or donor-acceptor bonds, which cause the formation of solvated complexes.

Two functional groups participate in the formation of a hydrogen bond; one of them is a proton donor (acid group), while the other, a proton acceptor (base group). The following classification of compounds according to the type of hydrogen bonds is accepted:

Class of compounds	Proton donor group	Proton acceptor group
A	Yes	No
B	No	Yes
AB	Yes	Yes
N	No	No

Class A consists of compounds which contain only proton donor groups. They include halogen-containing compounds in which the number of halogen atoms is enough for activating hydrogen: $CHCl_3$, $CHBr_3$, CH_2Cl_2, etc. The CH groups of acetylene and phenyl acetylene may enter into a hydrogen bond. Polyvinyl chloride and polychloroprene are among polymers which belong to this class.

Class B consists of compounds which contain only proton acceptor (or electron donor) groups: ketones, aldehydes, ethers, esters, tertiary amines, olefins, benzene and other aromatic compounds; proton acceptors are O, N and F atoms. Polytetrafluoroethylene, polyvinyl acetate, polyacrylates and others contain proton acceptor groups.

Class AB consists of compounds containing both proton donor and proton acceptor groups: alcohols, acids, amides, oximes, primary and secondary amines, and water. They also include cellulose, polyvinyl alcohol, polyacrylic and polymethacrylic acids, and polyamides.

Class N consists of compounds which do not have groups capable of forming hydrogen bonds; they are CS_2, CCl_4 and saturated hydrocarbons *.

The ability of compounds to form a hydrogen bond is closely connected with their ability to mix with one another. For example, the compounds of Class N mix well with one another and considerably worse with compounds of other classes, especially of Class AB. For such substances, the main type of interaction is dispersion interaction (p. 94).

Molecules of the compounds of Class A and Class B cannot form hydrogen bonds with molecules which are similar to them. For

* It has recently been shown that hydrogen of methylene groups is capable of entering into weak hydrogen bonds.

example, hydrogen bonds are absent in chloroform or acetone. But these substances form hydrogen bonds with one another. Polymers possessing only proton donor or only proton acceptor groups are not associated, but they can form hydrogen bonds with liquids of Classes A, B and AB. Polymers containing both types of groups are also capable of dissolving in liquids of classes A, B and AB, and everything depends on the strength correlation of the hydrogen bonds of polymer-polymer, polymer-solvent and solvent-solvent contacts, i.e., everything depends on the partner. For example, polyvinyl alcohol, which belongs to Class AB, is capable of reacting with both water and lower alcohols, but its ability to dissolve in these liquids depends on temperature.

In addition to the hydrogen bond, the donor-acceptor, or coordination, bond is of great importance in polymer dissolution, being a certain type of a chemical bond which is formed if one component is capable of giving off an electron pair while another has free orbits for taking it. Solvents which give away an electron pair are known as donors, while those taking them, as acceptors.

The ability of a solvent to act as a donor is characterized by a donor number which is determined with respect to a certain standard acceptor. Table 12.2 gives the donor numbers of some solvents determined with respect to $SbCl_5$ and the values of their dipole moments and the dielectric constant.

It follows from the table that the commonly used solvents have donor numbers which are smaller than those of water. But there are many liquids having considerably greater donor numbers, and it is precisely they which are good solvents of difficultly soluble polymers: polyvinyl chloride, polyvinyl alcohol, polyparabenzamide, etc. Donor numbers depend on the partner, and the order of solvents may change if another acceptor substance is taken. But there is evidently no correlation between donor numbers, the dielectric constant and the dipole moment. Therefore, the solubility of polymers of a more complex structure (polyamides, polyurethanes, etc.) is not and cannot be in correlation with the values of μ and ε of a solvent, and this was shown earlier.

Aromatic polymers are capable of forming pi-complexes, i.e., complexes constituted by mobile pi-electrons of aromatic rings and by free orbitals of solvent molecules, including molecules of aromatic solvents. This explains the good solubility of polystyrene in aromatic hydrocarbons and in some chlorine derivatives (tetrachloroethane, chloroform).

The foregoing indicates the exceptionally complex nature of the polymer-solvent interaction, which, in addition, depends on the shape and size of macromolecules, i.e., on their ability to undergo conformation transformations in respect of their molecular mass, packing density and other factors.

Molecular Mass of Polymers. The ability of a polymer to dissolve always decreases as its molecular mass increases in any polymer homologous series. Low-molecular members of a series can dissolve infinitely in a given liquid, while high-molecular ones can swell only finitely. This is due to great energies of interaction created along the entire chain length and to the finite mobility of chain units interconnected by chemical bonds. The different ability of polymer homologues to dissolve is used for their separation into fractions (p. 365).

Flexibility of Polymer Chain. The mechanism of dissolution of a polymer consists in separation of the chains from one another and their diffusion into the solvent. Both processes depend on chain flexibility. If the chains are flexible, they can move in parts by successive displacement of groups of units or segments (p. 101). Then there is no need to spend energy on separating two chains over their entire length simultaneously. It is sufficient to separate small sections of adjacent chains from one another. This requires a small amount of energy, offset by the intersection energy of the chain units with the solvent molecules. For this reason flexible-chain polymers, which are, as a rule, nonpolar, are usually miscible with nonpolar liquids.

Rigid chains cannot move by parts, and therefore separation of two rigid chains from each other requires a large amount of energy. At ordinary temperatures the energy of interaction of the units with the solvent molecules is not high enough to separate the chains completely. Amorphous linear polymers, the rigidity of whose chains is due to the presence of polar groups, swell readily in strongly polar liquids, but do not dissolve in them, as a rule, at ordinary temperatures. To dissolve very stiff polymers there must be a strong interaction between polymer and solvent (e.g., cellulose dissolves in quaternary ammonium bases, and polyacrylonitrile in dimethylformamide).

Packing Density of Macromolecules. Since the energy of interaction depends on intermolecular distance (p. 94), a looser packing of polymer molecules leads to weaker interchain interaction and better polymer solubility. The good solubility of polystyrene and the high solubility of some cardo polymers, for example, are connected with this.

Heterogeneity in Respect of Chemical Composition. The chemical composition of many polymers differs, depending on the conditions of their preparation. For instance, different samples of cellulose acetate may have different degrees of acetylation, samples of cellulose nitrate may differ in degree of nitration, samples of poly(vinyl alcohol) may contain different amounts of unsaponified acetyl groups, etc. Such polymers differ in solubility because their chains contain different functional groups ($OCOCH_3$ and OH, or

OH and ONO_2). For example, cellulose triacetate is soluble in methylene chloride and glacial acetic and formic acids but is insoluble and does not swell in hydrocarbons and is only partially miscible with ketones and esters. Cellulose acetate containing about 54-57 per cent acetyl groups is miscible with acetone and other ketones. Cellulose nitrate containing 10-12 per cent nitrogen is miscible with acetone, but cellulose trinitrate only swells in it insignificantly. Neither of these nitrates interacts with water or hydrocarbons.

Crystalline Structure of a Polymer. To make crystalline polymers dissolve, it is necessary to destroy the crystalline lattice, and this requires great energy. Hence, at room temperature crystalline polymers are, as a rule, insoluble even in liquids of similar polarity. For instance, at 20 °C polyethylene swells limitedly in *n*-hexane but dissolves in it only when heated. Isotactic crystalline polystyrene will not dissolve at room temperature in solvents suitable for atactic polystyrene: it also has to be heated to make it dissolve. Polytetrafluoroethylene is insoluble in all known solvents at all temperatures.

Chemical Crosslinks. Even a small number of chemical crosslinks between chains prevents them from separating and passing into solution. To make a polymer insoluble it is sufficient to create at least one bond between each two chains; for example, vulcanization of rubber with sulphur requires 1 mole of sulphur for every 2 moles of polymer. This means that a rubber with an average molecular mass of 100 000 requires 32 g of sulphur for every 200 000 g of rubber, or about 0.16 g of sulphur per kilogram of rubber. The presence of 0.08 g of oxygen per kilogram of a rubber capable of reacting with oxygen to form crosslinks is sufficient to make the rubber insoluble. Thus, insignificant amounts of crosslinking additives completely deprive polymers of solubility in any solvents. Crosslinked polymers do not become soluble, no matter what temperature they are heated to.

If the amount of crosslinks in the polymer is comparatively small, i.e., the network chains are fairly long, the molecules of low-molecular substances may penetrate into the polymer phase. This is accompanied by the prying apart of the sections of adjacent chains, and therefore a crosslinked polymer may swell to a limited extent Increasing the crosslink density decreases the ability of the polymer to absorb a low-molecular liquid; when its network chains become very short, the polymer completely loses its ability to swell. This can be illustrated by a number of examples. Thus, the ability of rubber vulcanizates to swell decreases continuously with increasing sulphur content. Ebonite, a vulcanizate containing about 32 per cent sulphur, does not swell at all Resolic phenol-formaldehyde polymers of linear structure dissolve readily in ace-

tone and alcohol. Resitol, a product of network structure, swells only limitedly in these solvents, and resite does not swell in them at all.

Temperature. The solubility of a polymer may improve or grow worse with increasing temperature. In this same temperature range some polymers will dissolve better when heated, others, when cooled, in the same solvent.

The effect of temperature will be discussed in more detail below.

12.1.6. Phase Equilibrium of Polymer-Solvent System

The phase rule is the basic law of equilibrium formulated by Gibbs for heterogeneous systems. The phase rule establishes the mutual relationship between the number of phases r, the number of components n and the number of degrees of freedom Φ of a system:

$$\Phi = n + 2 - r \tag{12.3}$$

The number of components of a thermodynamic system is the smallest number of individual substances that can form all the phases of the system.

The number of degrees of freedom shows how many thermodynamic variables determining the state of the system (pressure, temperature, etc.) can be varied arbitrarily without changing the number of phases in the system, i.e., without disturbing its equilibrium. The phase rule is applicable only to reversible systems at equilibrium and, conversely, applicability of the phase rule is the criterion of reversibility and thermodynamic stability of a system.

The properties of condensed systems (systems containing only liquid and solid components) are affected insignificantly by changes of pressure, and therefore in such systems pressure may be considered constant; then Eq. (12.3) becomes

$$\Phi = n + 1 - r \tag{12.4}$$

According to Eq. (12.4) a two-component one-phase condensed system has two degrees of freedom (the state of the system is determined by its temperature and the concentration of one of its components).

With two phases ($r = 2$), a condensed two-component system has one degree of freedom. This means that a change in temperature will cause a change of concentration in both phases, but at a certain temperature these phases may mix together, forming a one-phase homogeneous solution. Conversely, a one-phase homogeneous solution at a certain temperature is separated into two phases. Two cases are possible: (a) one liquid phase is separated into two liquid phases, and (b) a component in crystalline form is isolated from a liquid phase. The first type of separation is known as *liquid-liquid separation*, and the second type, as *liquid-solid se-*

paration. In the first case, the number of phases changes, while the phase itself does not change; in the second case, the number of phases and the phase itself change.

A solution of every concentration separates at a certain temperature, which is known as the *temperature of phase separation* $T_{p.s}$. The dependence of $T_{p.s}$ on phase composition is described by a *coexistence curve* or *phase diagram.* All the points on the curves of phase diagrams are obtained under equilibrium conditions, i.e., the state of a system does not depend on the way of attaining equilibrium. Therefore, the applicability of the phase rule is a criterion of the reversibility and thermodynamic stability of a system.

The first studies in which the phase rule was applied to polymer solutions were carried out in 1912. The objects of study were proteins: egg and serum albumins, and gelatin. The most important works in this field were those of Sorensen and McBain, who studied the salting out of proteins and gelatin from aqueous solutions with Na_2SO_4, $(NH_4)_2SO_4$, KNO_3, $NaNO_3$, and other salts. Knowing the number of components and the number of phases, they calculated the number of degrees of freedom for the systems studied from Eq. (12.3). This led to the conclusion that solutions of gelatin are "thermodynamically stable in the sense in which crystals or solutions of sugar and salt are stable". Despite these indications, solutions of gelatin, like those of other polymers, were for a very long time considered colloidal, aggregatively and thermodynamically unstable systems. These ideas were subsequently refuted, however, and phase diagrams have been obtained for many polymer-solvent systems.

Binary Systems. The first sign of separation of a homogeneous clear system into two phases or the formation of a new phase is the slight clouding of a system (opalescence). It is the result of light scattering by very fine particles of a phase that is being newly formed. This is the basis of the method of obtaining a phase diagram proposed by V. F. Alexeyev, being known as the *cloud-point method.* It consists in very slow alternate heating and cooling of solutions of a given concentration and in the registration of $T_{p.s}$ as a solution becomes cloudy and clear. Then, a graph of dependence of certain $T_{p.s}$ on composition is plotted; it is expressed in the mole, weight or volume fractions of components.

The molar fraction of a component of a binary solution is calculated from the equation *

$$N_2 = \frac{n_2}{n_1 + n_2} = \frac{\frac{g_2}{M_2}}{\frac{g_1}{M_1} + \frac{g_2}{M_2}} \tag{12.5}$$

* The subscript 2 stands for polymer and the subscript 1, for the low-molecular component.

where n_1 and n_2 = numbers of moles of first and second components in solution
g_1 and g_2 = weights of first and second components
M_1 and M_2 = molecular masses of components

Since the molecular mass of polymer M_2 is a very large value, the numerator of the fraction in Eq. (12.5) is small. Hence, even in solutions containing a large mass of polymer its molar fraction is very small and the molar fraction of the low-molecular component is close to unity. For this reason in polymer solutions the concentration of components is not expressed in molar fractions, but in weight or volume fractions.

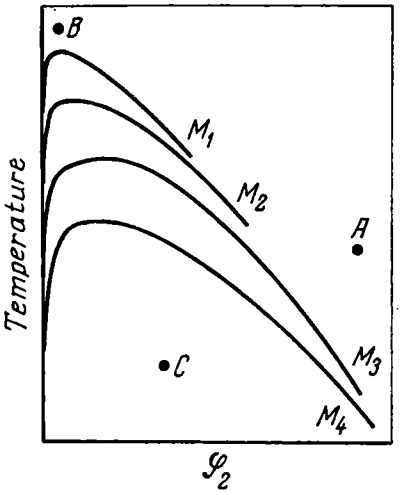


Fig. 12.2. Dependence of upper critical temperature on molecular mass of polymer ($M_1 > M_2 > M_3 > M_4$)

The *weight fraction of a component* is the ratio of its weight to the sum of weights of all the components:

$$\omega_1 = \frac{g_1}{g_1 + g_2} \qquad \omega_2 = \frac{g_2}{g_1 + g_2} \tag{12.6}$$

The *volume fraction of a component* is the ratio of its partial molar volume to the total volume of solution:

$$\varphi_1 = \frac{\bar{V}_1}{\bar{V}_1 + \bar{V}_2} \qquad \varphi_2 = \frac{\bar{V}_2}{\bar{V}_1 + \bar{V}_2} \tag{12.7}$$

Obviously,

$$\omega_1 + \omega_2 = 1 \quad \text{and} \quad \varphi_1 + \varphi_2 = 1 \tag{12.8}$$

In some cases the molecular mass of monomeric unit M_u is used in Eq. (12.5) instead of the molecular mass of polymer for calculating the molar fraction:

$$N_1 = \frac{\frac{g_1}{M_1}}{\frac{g_1}{M_1} + \frac{g_2}{M_u}} \tag{12.9}$$

The concentration of a polymer in the solution is also expressed by the number of grams dissolved in 100 ml of the low-molecular liquid (g/100 ml).

The first phase diagrams of binary polymer-solvent systems were obtained by Kargin, Rogovin, and Papkov.

Figure 12.2 is a typical phase diagram of a binary polymer-solvent system with an *upper critical solution temperature* (UCST). The point corresponding to this temperature is the peak of the coexistence curve. Such systems are similar to the phenol-water system, for instance, but differ from it in that the coexistence cur-

ves are displaced greatly towards low concentrations of one of the components, namely, of a polymer. Hence, the critical concentration of a polymer is very low. It depends on the molecular mass of a polymer, decreasing with increasing molecular mass, while the critical temperature rises.

The coexistence curve separates the region of unlimited miscibility from that of limited miscibility. At a given temperature any point situated above the curve (e.g., *A* or *B*) corresponds to the concentration of a homogeneous solution. Points in the region beneath the curve (e.g., *C*) correspond to a microheterogeneous two-phase system which separates in time into two clear layers in equilibrium with each other. The composition of these layers can be found by drawing an isotherm for each temperature. It will intersect the coexistence curve at two points, the abscissas of which correspond to the volume fractions of the second components in each layer.

Raising the temperature changes the concentrations of the components in both layers, bringing them closer together, but each temperature corresponds to a definite solubility of one liquid in the other. At the critical temperature the compositions of both phases become the same, the interface between them disappears, and a homogeneous solution results.

Upper critical solution temperatures have been found for the systems cellulose acetate-tetrachloroethane, cellulose acetate-chloroform, polyisobutylene-benzene, polystyrene-cyclohexane, polystyrene-decalin, and others. In these cases the solubility of polymers improves with rising temperature.

However, in some polymeric systems the miscibility of the components improves with declining temperature, and phase separation occurs on heating. These systems, an example of which is triethylamine-water, are characterized by a *lower critical solution temperature* (LCST). This temperature corresponds to a minimum on the coexistence curve.

There are two types of LCST. The first type of LCST, which is the more common one, is characteristic of systems in which strong hydrogen bonds form between the component molecules, promoting mixing of the components. When heated these bonds are broken by thermal motion, worsening the miscibility of the components. The LCST of such systems is below the boiling point of the solvent, and the higher the molecular mass of the dissolved polymer, the lower will be the LCST. An example are aqueous solutions of oligomeric polyhydroxypropylenediols and polyhydroxyethylenediols.

The phase diagrams of many polymeric systems have not been obtained, but it is known, for instance, that the miscibility of components grows worse on heating. This is observed for the systems:

cellulose-water, methyl cellulose-water, ethyl cellulose-water, cellulose nitrate-ethanol, etc.

The second type of LCST, detected recently by Freeman and Rowlinson, is observed in systems whose components are close in chemical constitution, but differ in the size of their molecules. The specific feature of this type of LCST is that it lies above the boiling point of the more volatile component, between its T_b and the critical temperature of its transition from liquid to gas (L-G). This kind of LCST has been detected in the systems ethane-dodecane, decane-$C_{24}H_{50}$ and $C_{37}H_{76}$, and for many polymeric systems, namely, polyisobutylene-polyethylene, polypropylene-*n*-alkanes, 1-polyoctene-*n*-pentane, poly(vinyl acetate)-ethylacetate, cellulose acetate-acetone, poly(vinyl alcohol)-water, polystyrene-benzene and ethylbenzene.

Theory predicts that any polymer-solvent system should have both an upper and a lower critical solution temperature; their values for some systems are listed in Table 12.3. Figure 12.3 shows

TABLE 12.3. *Upper and Lower Critical Solution Temperatures of Some Polymer-Solvent Systems*

System	Upper critical solution temperature, °C	Lower critical solution temperature, °C
Polystyrene-cyclohexane	30	180
Polystyrene-cyclopentane	6	150
Polyisobutylene-benzene	23	160
Poly(vinyl acetate)-ethyl acetate	—	206
Polystyrene-benzene	—	241
Polystyrene-ethylbenzene	—	295

schematically three different types of phase diagrams of polymer-solvent systems. In the first case (Fig. 12.3*a*) UCST > LCST, and complete miscibility is observed at component ratios corresponding to points outside the curve. An example is the system poly(ethylene oxide)-water. In the second case (Fig. 12.3*b*) LCST > > UCST, and the region of complete miscibility lies between the curves. The higher the molecular mass of the dissolved polymer, the smaller will be this region. Finally, a third case is possible (Fig. 12.3*c*), where there is no region of complete miscibility at all. Figure 12.4 shows the phase diagrams of a number of polymeric systems.

Since CST depends on the molecular mass of a polymer, a phase diagram should be determined for monomolecular polymers. Real polymers are polymolecular, being multicomponent systems. The

cloud-point curves of their solutions usually have inflection (Fig. 12.5). Köningsveld and Flory have shown that the maximum of the cloud-point curve in this case does not correspond to the critical point, which was found by the method first proposed by Konovalov. The method consists in measuring the volumes of coexisting phases, whose ratio in the critical point should always

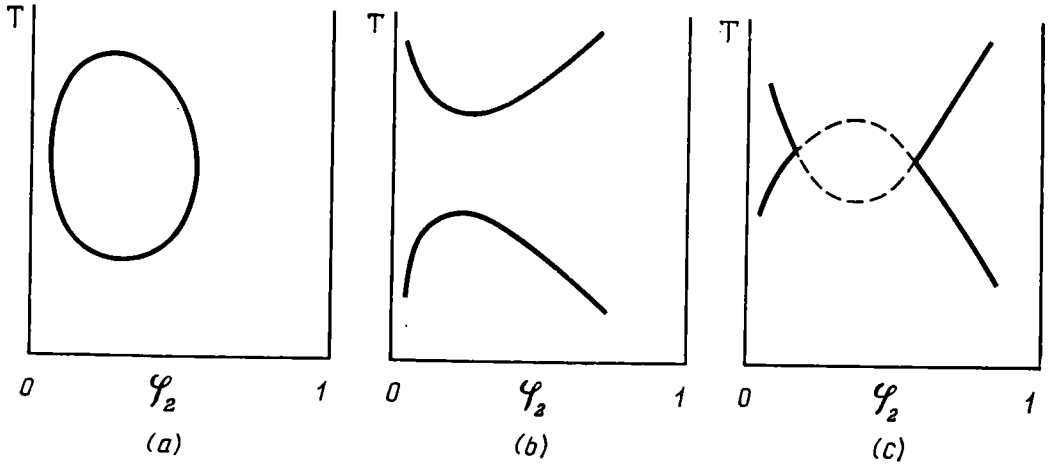


Fig. 12.3. Typical coexistence curves for polymer-solvent systems: (*a*) UCST > LCST; (*b*) LCST > UCST; (*c*) no unlimited miscibility region

be equal to unity. The illustration shows that the critical point found by this method coincides with the point of inflection on the cloud-point curve.

Figure 12.6 gives a phase diagram which is characteristic of liquid-solid separation. It resembles a phase diagram of metal alloys. However, due to the great difference in the dimensions of molecules of the components being mixed together, only the right branch of a diagram may be observed for polymer solutions; in essence, this branch is the *liquidus* line. The region above the curve corresponds to one-phase system, and that under it, to the two-phase system: *a swollen polymer* and its crystals.

The presence of a crystalline phase in such a swollen precipitate is sometimes detected directly by X-ray method. However, in some cases, crystal particles which have been isolated are so small that they cannot be detected by the structural analysis. A phase diagram of the kind shown in Fig. 12.6 is the evidence of liquid-solid separation. It is evident from such diagrams that the phase compositions cannot become equal at any temperatures; it follows that such systems do not have a critical solution temperature.

Phase diagrams of a more complex nature are observed for some polymer-solvent systems. For example, liquid-liquid separation may be observed in one concentration region, and liquid-solid sep-

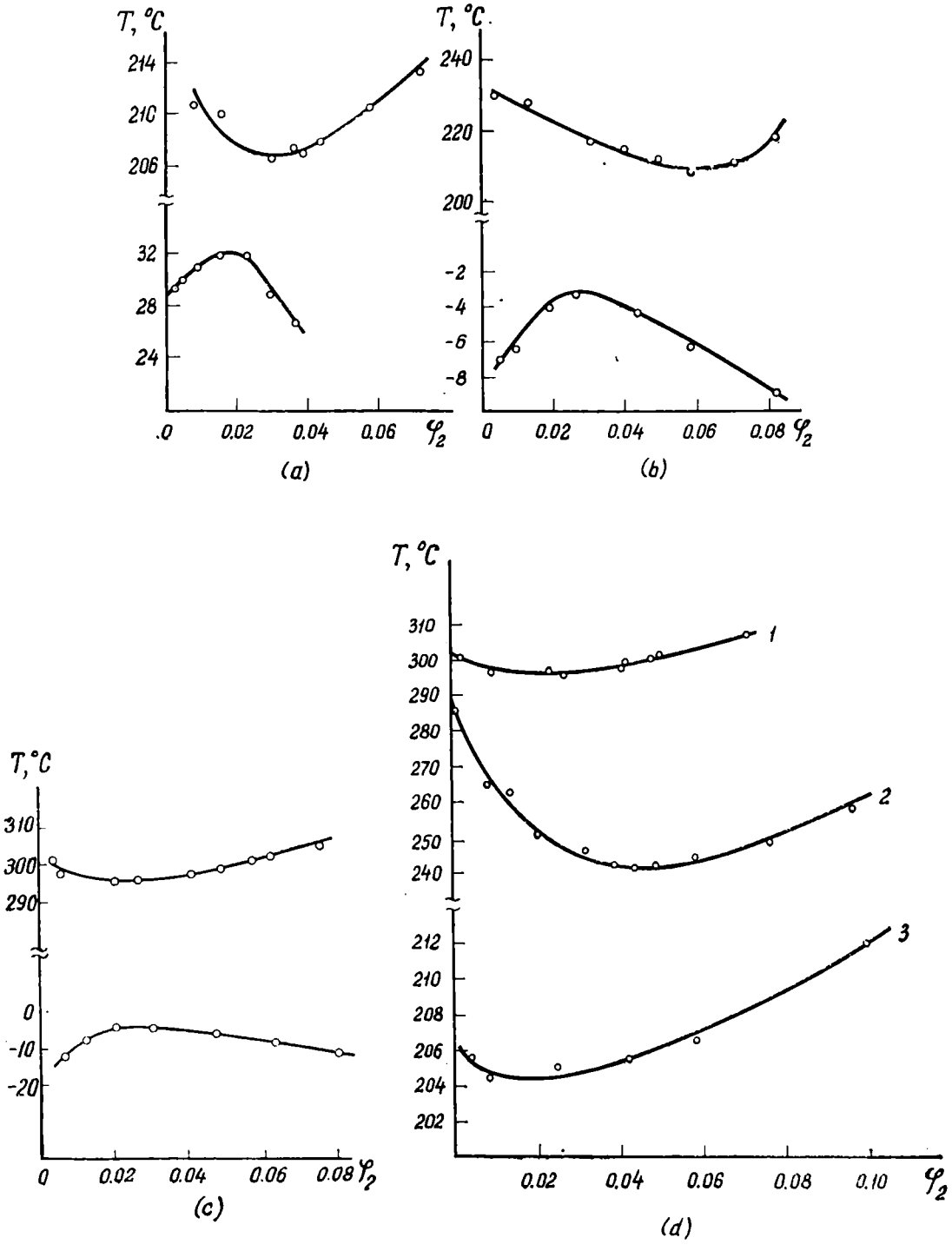


Fig. 12.4. Phase diagrams of systems:
(*a*) polystyrene-cyclohexane; (*b*) poly(vinyl acetate)/ethyl acetate; (*c*) polystyrene-ethylbenzene; (*d*) *1* — polystyrene-ethylbenzene, *2* — polystyrene-benzene, *3* — poly(vinyl acetate)/ethyl acetate

aration, in another. This has been noticed for solutions of crystalline polypropylene in some liquids. Aqueous solutions of polyvinyl

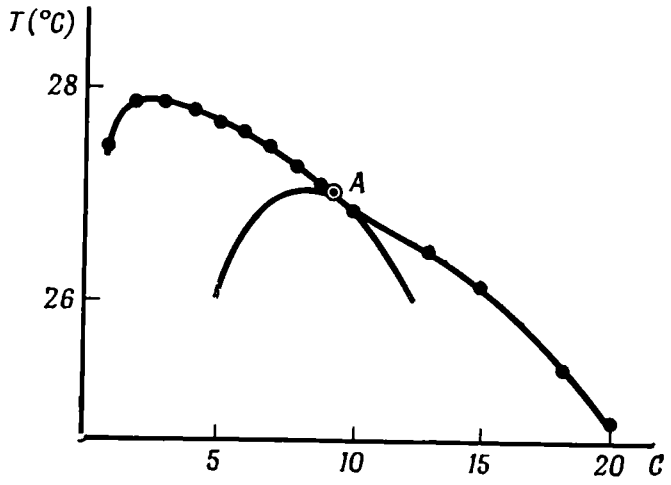


Fig. 12.5. Typical phase diagrams of liquid and crystalline separation of phases (explanation is given in the text)

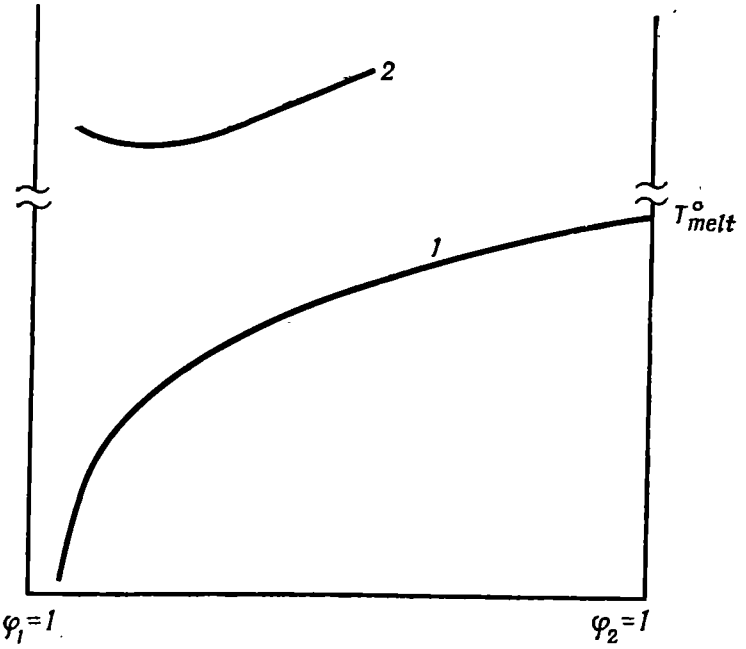


Fig. 12.6. Phase diagram of crystalline polymer solutions:
1—liquidus line; *2*—liquid separation (LCST)

alcohol and its derivatives are characterized by liquid-solid separation in the low-temperature region and by liquid-liquid separation, in the high-temperature region.

Ternary systems. The compositions of ternary systems at constant temperature are represented graphically by equilateral triangles (Fig. 12.7). The vertices of the triangle correspond to 100 per cent content of the components *A*, *B*, and *C*. Points on the

sides of the triangle correspond to compositions of the binary mixtures *A-B*, *B-C*, and *A-C*. The composition of a ternary mixture is represented by a point lying inside the triangle, e.g., by the point *O*. The sum of the intercepts $Oa + Oc + Ob$ of lines drawn through this point parallel to the sides of the triangle is always equal to a side of the triangle, i.e., to unity. The intercepts *Oa*, *Oc*, and *Ob* correspond to the fractions of the components *A*, *C*, and *B* in the mixture.

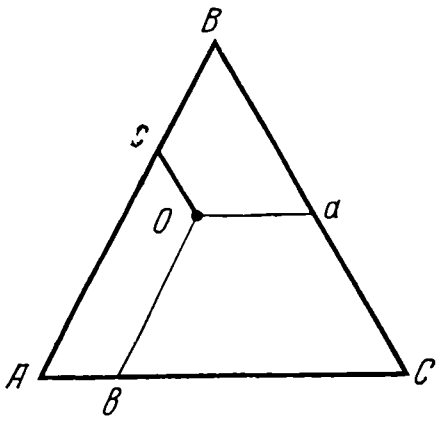


Fig. 12.7. Phase diagram of a ternary system at constant temperature

To plot such a diagram, an exactly weighed portion of a polymer is dissolved in a certain amount of a good solvent, and then a poor solvent of this polymer is gradually added to the clear solution until stable cloudiness appears. Knowing the amount of all three components in the mixture that has been formed, their fractions are plotted on a side of a triangle. Then, lines parallel to the sides of the triangle are passed through these points. The point of their intersection corresponds to the composition of a solution. Brönsted was first to obtain the phase diagrams of the polymer-liquid I-liquid II systems. They have the form shown in Fig. 12.8. The size of the region of complete miscibility depends on the nature of the components. Thus, if we take two liquids, of which the polymer swells unlimitedly in one and to a limited extent in the other, the region of complete miscibility is large (Fig. 12.8*a*). If the polymer swells unlimitedly in one liquid and does not interact at all with the other, the region of complete miscibility will be small (Fig. 12.8*b*). This region is still smaller if the polymer swells to a limited extent in one liquid and does not interact in the other (Fig. 12.8*c*). If the polymer swells to a limited extent in both of the liquids taken, two cases are possible, as shown in Fig. 12.8*d* and *e*.

Especially interesting is the instance represented by Fig. 12.8*e*, which indicates that the addition of *n*-propyl laurate to polystyrene swelled in acetone results in the formation of a homogeneous solution with an extensive region of complete miscibility. However, the addition of large amounts of *n*-propyl laurate causes phase separation again. Hence, it has been frequently observed that certain polymers can be readily dissolved in mixtures of two or more solvents, whereas they are not soluble in the individual components of the mixture. This phenomenon, known as *cosolvency*, is of great practical importance and has been studied frequently in a qualita-

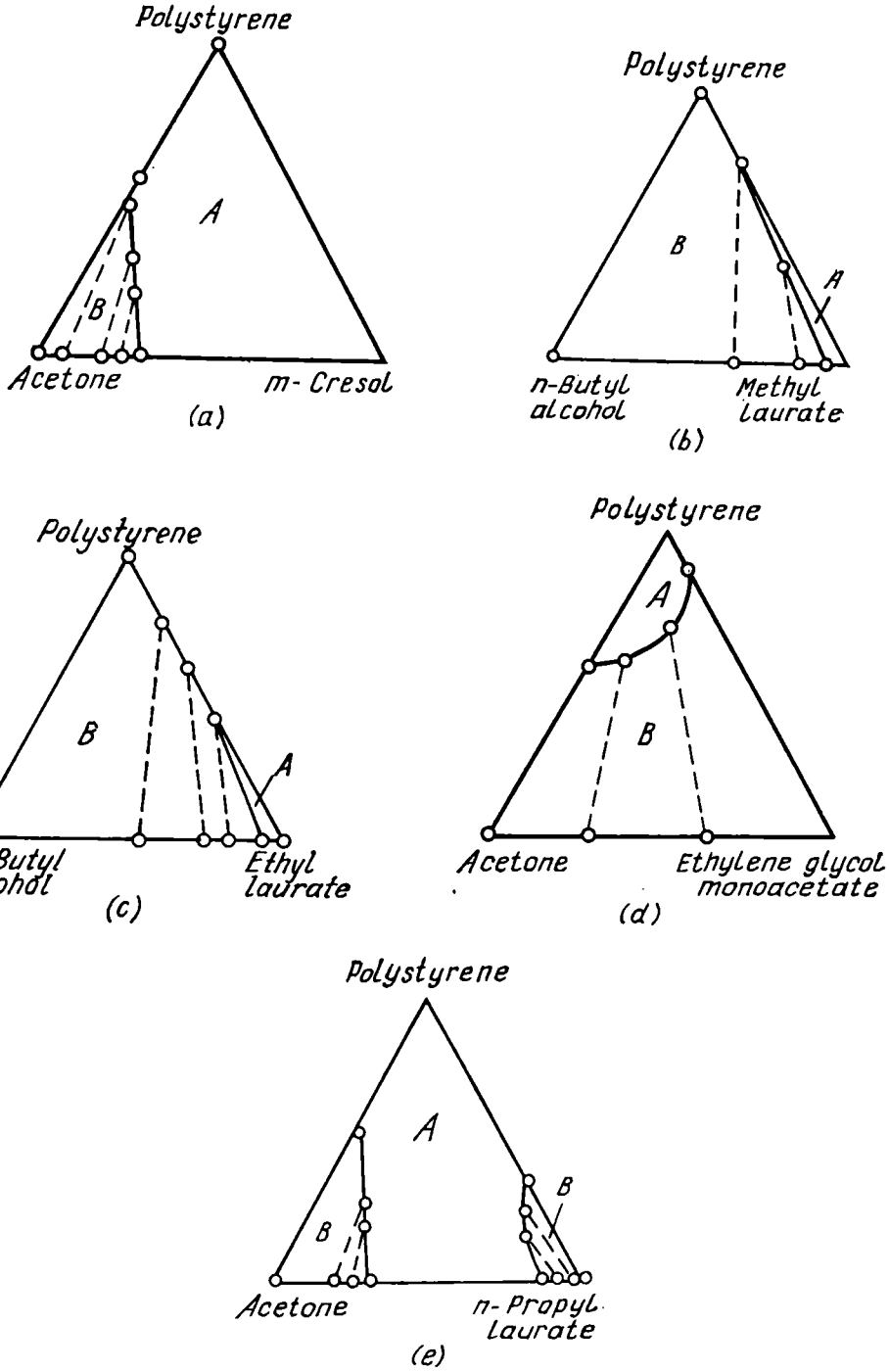


Fig. 12.8. Ternary phase diagrams of:

a — polystyrene/*m*-cresol/acetone; *b* — polystyrene/methyl laurate/*n*-butyl alcohol; *c* — polystyrene/ethyl laurate/*n*-butyl alchohol; *d* — polystyrene/ethylene glycol monoacetate/acetone; *e* — polystyrene/*n*-propyl laurate/acetone; *A* — region of complete miscibility; *B* — region of partial miscibility

tive manner from the industrial point of view. Such mixtures are often used in practice. For instance, cellulose nitrate containing 10-12 per cent nitrogen swells to a limited extent in ethyl alcohol and ethyl ether. A mixture of these liquids taken in definite proportions dissolves cellulose nitrate unlimitedly, and this is utilized for the preparation of collodion.

The ternary diagram method is widely used for studying systems containing a polymer and two low-molecular liquids (polymer-liquid I-liquid II), and also more complex systems containing two different polymers and one low-molecular liquid (polymer I-polymer II-liquid).

The entire given material shows that the polymer solutions formed spontaneously are thermodynamically stable equilibrium systems. They are true solutions. However, equilibrium in polymer solutions is established very slowly due to the presence of very large macromolecules, which have low mobility and great relaxation times.

To each temperature corresponds a strictly definite concentration of both coexisting phases, i.e., a definite state of equilibrium. Variation of temperature changes the concentration of the phases, involving transition of macromolecules from one phase into the other. This passage takes time and the more so, the higher the concentration of the solution. Consequently, when the temperature changes, a new equilibrium is not established instantly in polymer solutions, but is reached only after a comparatively long time. Hence, to assess the properties of polymer solutions correctly, their changes should be studied in time, and only data that have reached constant values may be considered valid.

12.2. GELS OF POLYMERS

The gels of polymers are very important systems. They are of great significance in the food industry and industries of photographic materials, man-made fibres and in some other branches of technology, and also to *living organisms*.

A gel is a polymer-solvent system with a network of sufficiently stable bonds which are not destroyed by thermal motion, i.e., a network of a *non-fluctuation* nature. This is mainly what distinguishes a gel from a solution.

A gel passes over to the solution if, upon a change in temperature, the crosslinks in a network become weaker and may be destroyed by thermal motion, i.e., the network becomes fluctuational. This process is known as gel *melting*.

There are two types of gels. The **gels of type I** are polymer-low-molecular liquid (LML) systems in which the network is formed by chemical bonds between molecules. The bonds are not destroyed on heating, and such gels do not melt at any temperature. When

such gels are heated to a temperature higher than a certain one, the entire system is irrecoverably destroyed thermally. Therefore, such gels are called *thermally irrecoverable.*

The **gels of type II** are systems in which the network is formed by intermolecular bonds of a different nature. These bonds are stable under certain conditions, but they may rupture when conditions (temperature, the nature of LML, etc.) change. In this case, a homogeneous true solution is formed. When the system returns to the initial conditions, strong interchain bonds are again formed; the *system gelates.* Such gels are said to be *thermally recoverable* or *elastic.*

The **gels of type I** are formed:

(1) in the case of the spontaneous swelling of crosslinked polymers;

(2) in the case of three-dimensional polymerization or polycondensation in a solution;

(3) during chemical reactions of crosslinks in the presence of a solvent.

Gels formed by chemical bonds are incapable of flowing, since macromolecules, being crosslinked, cannot move relative to one another. The moment when a system loses fluidity during polymerization or polycondensation in a solution and passes over from a viscous to a gel-like state is known as the *gelation point*, or the *gel point.*

An example of the gels of type I is the swollen vulcanizates of rubbers, the swollen crosslinked copolymers of styrene and divinyl benzene, and so forth. They swell spontaneously, as a result of which equilibrium thermodynamically-stable one-phase gels are formed. The equilibrium degree of swelling depends on the degree of crosslinking of a polymer, the temperature, and the nature of a solvent.

Figure 12.9*a* gives a typical phase diagram of the gel of type I, which has been obtained when a crosslinked polymer became swollen in a liquid that was a poor solvent for its noncrosslinked analogue. Every point on the straight line corresponds to the equilibrium degree of polymer swelling at a certain temperature, i.e., to the existence of equilibrium one-phase gels. The higher is the temperature, the larger is φ_1^{equil} and the smaller is φ_2^{equil}. Since a crosslinked polymer does not dissolve, the coexisting phase is a pure LML at all temperatures. The region that is to the right of the curve corresponds to the existence of nonequilibrium one-phase gels, which may still absorb liquid at a given temperature. The better is the solvent, the greater is the equilibrium degree of swelling, all other conditions being equal, and the more is the curve displaced to the left.

Such phase diagrams are observed up to the boiling temperature

of LML (if T_{boil} is lower than the temperature of chemical degradation of a polymer). However, under special conditions, swelling may be carried out at a temperature higher than T_{boil}. In this case, a complete analogy is observed in the behaviour of a crosslinked polymer and of a noncrosslinked polymer which is analogues to it. Hence, it follows from Fig. 12.4*a* that a solution of polystyrene in cyclohexane separates on cooling and heating. Figure 12.9*b* shows that the degree of swelling of crosslinked polystyrene in the low-temperature region grows with a rise in temperature, and in the

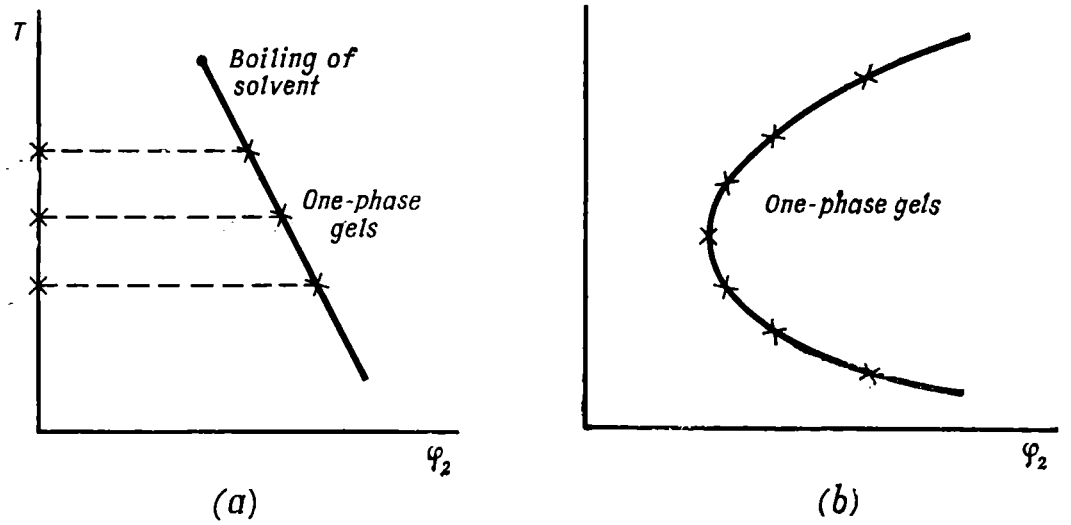


Fig. 12.9. Phase diagrams of gels of type I (explanation is given in the text)

high-temperature region it diminishes. But the gel does not melt even in this case. In the entire temperature region, the coexisting phase is pure LML. It follows that the gels of type I cannot possess critical solution temperatures.

If a gel formed upon swelling at a higher temperature is cooled, some liquid will be separated from it, and its content in the gel will correspond to the equilibrium degree of swelling at a new, lower temperature. The process of the visible separation of LML from the gel is known as *syneresis* or macrosyneresis. It is observed also during the formation of a network in a solution, when the LML concentration is considerably greater than equilibrium concentration, which corresponds to the given degree of crosslinking. In this case, the gel is a nonequilibrium two-phase system in which syneresis occurs until an equilibrium state is established. Hence, at temperatures lower than the polymer degradation temperature, the gels of type I behave as reversible equilibrium systems.

The **gels of type II** are formed during the interaction of linear or branched polymers having diphilic groups (which differ from one

another in polarity) with solvents which are not very good thermodynamically (p. 389) and which interact only with one type of groups and do not interact with another. Gels are as a rule not formed in the medium of a very good solvent of a given polymer. Therefore, gelation occurs when conditions change, worsening the solvency of a medium. This may take place when temperature changes or when a poor solvent is added to a polymer solution in a good solvent. In this case, the system may be expected to separate into two phases. But in many cases, such macroseparation does not occur due to kinetic hindrances, and a gel is formed. This

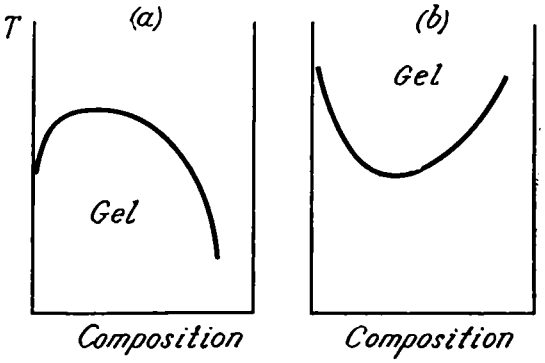


Fig. 12.10. Phase diagram of a gel of type II

is a *nonequilibrium* system, and the formation of two phases corresponds to its equilibrium state. Therefore, the gels of type II are *two-phase* gels. As S. P. Papkov rightly stated, they are systems with incomplete phase separation.

Figure 12.10 gives a phase diagram of a gel of type II. The left branch of the curve is obtained by the cloud-point method, by gradually cooling and heating a system. Opalescence appears due to *microseparation* or microsyneresis, i.e., the formation of microheterogeneities, which are light-scattering centres. The right branch of the curve is usually obtained when studying the equilibrium degree of swelling of a polymer specimen at different temperatures *.

To the right of the right branch of the curve is a region corresponding to one-phase nonequilibrium gels, which may absorb a certain amount of LML at a given temperature. They melt at a definite temperature. The region inside the curve corresponds to two-phase gels in which the syneresis process develops with time, i.e., the separation of a pure liquid phase or a very dilute solution is observed. Such a system should ultimately separate into two phases.

* It has been shown recently that the position of this branch, i.e., the equilibrium degree of swelling of specimens of gelatin and polyvinyl alcohol, depends on their prehistory.

A classical example of a two-phase gel is the gel of gelatin, which is formed when its solutions cool. The stable network is apparently created by bonds between the hydrophobic hydrocarbon parts of the adjacent protein macromolecules, which are not destroyed by water at ordinary temperatures. Two-phase gels are formed during the cooling of solutions of polyacrylonitrile in dimethyl formamide, and so forth.

If a polymer is capable of crystallization, the gel which is formed has a crystalline structure. This is observed, for example, during the cooling of solutions of polyvinyl alcohol in ethylene glycol or glycerin and to a lesser extent during the cooling of aqueous solutions of polyvinyl alcohol: Crystallization is always more perfect when the chemical nature of LML and that of a polymer chain unit are similar. The phase diagram of crystalline gels has the form presented in Fig. 12.6. The region under the curve *1* corresponds to a crystalline gel, whose turbidity increases in time as a result of continual crystallization and microsyneresis that it has caused; this microsyneresis may pass over to macrosyneresis.

Thermally recoverable gels are formed during the cooling of solutions of comb-like polymers which are being crystallized, e.g. solutions of a series of polyacrylates in aliphatic alcohols and hydrocarbons. In this case, stable bonds appear due to the interaction of methylene branches when their length is sufficiently large, and this creates an orientation order and leads to crystallization.

Hence, notwithstanding the different mechanisms of gelation in different systems, gelation is promoted by an intensification of interchain interactions and a diminution in the kinetic mobility of macromolecules.

Gelation may be caused by an addition of inorganic salts. It has long been known that the addition of salts to polymer solutions affects polymer solubility differently: in the presence of some salts, polymer solubility improves, and in the presence of others, it worsens and the polymer precipitates. The latter phenomenon has become known as the *salting out* of a polymer, and in the first case, the term *salting in* is occasionally used.

The worser solvency of a medium due to the addition of some salts often leads to gelation. This is observed when some salts are added to the solutions of cellulose acetate, the copolymers of methyl methacrylate and methacrylic acid, the solutions of polyvinyl alcohol and the products of its saponification, and so forth. The mechanism of salt action is complex and apparently varied. In some cases, salt-like chemical bridge bonds may form between chains. This may be observed when bivalent cations are introduced. However, univalent cations are also known to cause gelation. It has recently been shown spectroscopically that the OH and C=O groups in unaqueous polymer solutions are activated by the Mg^{2+}

cation, this, leading to the formation of stronger hydrogen bonds between them and to gelation.

It follows that the gels of type II are complex systems with different mechanisms of gelation.

12.3. COLLOIDAL DISPERSIONS OF POLYMERS

Spontaneous solution and swelling do not occur when there is no affinity between a polymer and a low-molecular liquid. However, colloidal dispersions may form in such systems. If a polymer is amorphous, such dispersions may be regarded as emulsions. For example, the milky juice of rubber-bearing plants, known as latex, is an emulsion. It is a system with drops or globules of rubber which are suspended in water. Polymer emulsions produced in emulsion polymerization are known as *synthetic latexes*. They are also aqueous dispersions of polymers.

A latex is a typical colloidal system with the following characteristic features: it is formed nonspontaneously and is aggregatively and thermodynamically unstable due to the presence of an interface between a disperse phase (drops of one liquid) and a dispersion medium. Therefore, the formation of such a system causes an increase in free surface energy, and the processes of coalescence occur in a system that has already been formed, being accompanied with a decrease in free energy and leading to the separation of the system. Like all colloidal systems, a latex is a two-phase system.

A stabilizer is needed to prevent coalescence and make a system stable. In a natural latex, stabilizers are various proteins whose molecules are adsorbed in the drop-medium interface. In synthetic latexes, a stabilizer is an emulsifier whose molecules are also adsorbed in the polymer-medium interface. Latexes obey all the regularities of colloidal systems.

True solutions and colloidal systems are extreme cases of strong and very weak interaction of a polymer with a low-molecular liquid. However, there may be intermediate cases.

12.4. PREPARATION OF POLYMER SOLUTIONS AND THEIR REFINING

The procedure of preparing polymer solutions is related to the specificity of their dissolution. Thus, the whole amount of solvent should never be added at once, because in this case a swollen envelope forms around the polymer fragment, making it difficult for the solvent to penetrate further into it. Passage of macromolecules from this swollen envelope into the solvent also occurs slowly, and this greatly retards the whole process of formation of a homogeneous solution. For this reason it is recommended to add at

first only some part of a solvent to cover the surface of the polymer with a thin layer. This causes swelling, which occurs faster than solution proper, and results in a continuous swollen transparent layer. Then the rest of the solvent may be added, while stirring, to bring the solution to the concentration desired; swelling passes spontaneously into solution.

Sometimes the polymer is not completely soluble and the liquid used as the solvent may be found to contain small pieces of the swollen crosslinked polymer, known as "gelites". They often have a refractive index close to that of the solvent, which makes it difficult to detect them visually. Taking this into account, completeness of solution must be checked carefully, for instance, by examining the solution in a bright beam of light. Any gelites found can be removed by filtering through close glass filters or by centrifuging.

However, the presence of insoluble particles is sometimes not definitive evidence that part of the sample has not dissolved. This may be due to slowness of the process of solution. If the solubility of polymers improves with rising temperature (p. 351), gentle heating will accelerate the disappearance of these particles. But solutions should be heated with care, because in a number of polymers this may cause additional crosslinking (p. 78), i.e., the formation of a three-dimensional network. Besides, it should be borne in mind that dissolved polymers are apt to oxidize and degrade. This may cause a radical change in properties of the solution. Therefore, polymer solutions should not be stored for long before investigation; sometimes they should even be stabilized by special substances inhibiting reactions between free radicals.

Since swelling involves the moving apart of chain macromolecules or more complex supermolecular structures, only intermolecular bonds are disrupted, and, as a rule, no chemical bonds are ruptured in the polymer chain. However, in a number of cases very high pressures develop in the swollen polymer (p. 385), which are capable of degrading it, i.e., rupturing its chemical bonds.

The time required to reach equilibrium in polymer solutions, i.e., the relaxation time, is affected considerably by electrolyte impurities, e.g., mineral salts, which are often present in polymers. The salts dissociate in aqueous solution and the resulting ions attract the polar groups of the polymer chains, forming intermolecular crosslinks between the chains. The presence of such crosslinks increases the relaxation time, hinders movement of the chains, and retards establishment of equilibrium. If the crosslinks are not very strong, the polymer dissolves; sometimes they are so strong that they prevent unlimited solution of the polymer. Therefore polymers containing mineral impurities should be thoroughly purified. This is done by dialysis and electrodialysis.

Dialysis is a separaiton process based on the fact that small ions pass through semipermeable membranes while large particles or large molecules remain behind.

If a polymer is insoluble in water, extraneous ions can be removed by washing the polymer repeatedly with bidistilled water. In the case of water-soluble polymers this can be achieved by using a semipermeable membrane which allows ions to pass through it but holds back polymer molecules, i.e., by means of dialysis. The simplest dialyzer is a bag made of a semipermeable material (e.g., cellophane), which is filled with an aqueous solution or suspension of the polymer and placed in a vessel with bidistilled water. Since the concentration of ions differs on either side of the membrane, the ions diffuse through it until their concentration levels out. The ions can be completely removed from the polymer by changing the water repeatedly.

Dialysis is a very slow process, and *electrodialysis* is now employed to speed it up. The polymer solution or suspension is poured into the middle cell of an apparatus called an electrodialyzer, and the side cells with electrodes fused into them are filled with water. The ions diffuse from the middle cell to the oppositely charged electrodes through a semipermeable membrane. Electrodialysis is carried out under a voltage of from 300 to 10 000 V. When high voltages are used, the water may become very hot and for this reason the side vessels are furnished with a cooling device. Since the concentration of ions in the side cells gradually increases during dialysis, tending to an equilibrium value, the water is periodically replaced. It should be noted that during dialysis low-molecular impurities with molecules smaller than the pores of the semipermeable membrane may diffuse into the water together with the electrolytes.

12.5. FRACTIONATION OF POLYMERS

As was indicated above, most polymers are polydisperse, i.e., are mixtures of polymer-homologues. It is sometimes necessary to separate such mixtures into fractions of more uniform molecular-mass distribution. Techniques for fractionating polymers are divided into preparative and analytical methods. In *preparative fractionation*, discrete fractions are obtained for further study. *Analytical fractionation* yields information about the distribution of molecular masses in a polymer without separating it into discrete fractions.

Many methods of preparative fractionation are known but the most popular are those based on the different solubility of polymers of different molecular mass.

A change in polymer solubility may be attained by varying the solvent action of a solvent. This is done by adding a poor solvent to a good one or by changing the temperature. Therefore, this method has three varieties: fractionation by precipitation, fractionation by solution and fractionation by lowering the temperature.

Consecutive Fractionation. A polymer specimen is dissolved in a suitable solvent until the formation of a clear solution. Theoretically, the effect of fractionation increases with a decrease in the concentration of a solution which is taken for precipitation. Therefore, 1 per cent solutions are usually prepared. A precipitant is gradually added to a solution at constant temperature while intensively stirring. After adding a certain amount of a precipitant, it is enough to add only one more drop of it to cause turbidity which does not disappear on stirring. This is the beginning of precipitation of the most high-molecular and consequently the least soluble fraction from a solution. After the appearance of stable cloudiness, stirring is ceased, the solution is allowed to stand at constant temperature, and the precipitate which has been formed is separated.

The remaining solution which contains all other fractions is treated in the same way, adding a precipitant to it until the next fraction is precipitated. In this way, many polymer fractions may be obtained, the last of which is the most low-molecular one. The precipitated phases, being different fractions, are dissolved in small amounts of a solvent and then poured out into a large amount of a precipitant while intensively stirring. In this case, a specimen of a fractionated polymer is produced in the solid form; it is then filtered off and dried to a constant weight at appropriate temperature in a vacuum.

Fractionation by Consecutive Dissolution. A specimen of a polymolecular polymer is consecutively treated with binary mixtures of liquids containing a decreasing amount of a nonsolvent, i.e., the solvency of a medium improves with every treatment of a solution. Therefore, the first fraction which dissolves is the most low-molecular one, and the last fraction which dissolves is the most high-molecular one. Like in the previous method, solutions containing different fractions of a polymer are poured into a large amount of a precipitant, and then they are separated from the liquid and dried. The method of direct extraction is occasionally used, i.e., a ground polymer is extracted in a flask or in a Soxhlet apparatus at appropriate temperature.

Fractionation with Decreasing Temperature may be employed when polymer solubility worsens as temperature drops. This method is advantageous, since a process occurs in the medium of only one solvent, the volume of a system virtually does not change, and so forth. However, it is difficult to select a solvent or even a sol-

vent-precipitant mixture in which fractionation would occur only when temperature changes. Therefore, among the three given varieties of the method, the first one is the most widely used.

Fractionation by Column Chromatography. This method consists in filling the column with inert material (packing) on which a layer of a polymer being fractionated is deposited and in passing the binary solvent-nonsolvent mixture (eluting mixture) through the column.

Inert material should have a sufficiently developed surface area. Glass spherules are usually employed for this purpose; their dimensions range from 40 μ to 70 μ. These spherules are placed in columns of different height in which the gradient of the eluting mixture concentration and the temperature gradient are created along the height. As a result, a polymer is fractionated; the first to be eluted being the fraction with the lowest molecular mass. In all, 10-25 fractions may be produced; they are isolated from solutions by different methods.

Gel-Penetrating Chromatography is a variety of the column fractionation method in which fractionation is effected by the molecular sieve method that is based on the ability of molecules to penetrate into the pores of an adsorbent of certain size. In the given method, adsorbents are materials which have no charges and ionogenic groups, with an exactly fixed pore size (p. 593). The best in this respect are specially prepared copolymers of styrene with divinyl benzene (p. 53), which form gels upon swelling (p. 226). Hence the name of the method. In addition, use is made of the gels of dextran (sefadex), varieties of silica gels (spherosil), and others.

A column is filled with small gel-like particles. One solvent is always used, and it should if possible dissolve different polymers. The best in this respect is tetrahydrofuran. A solution of a polymer in tetrahydrofuran is passed through a gel-filled column. High-molecular fractions do not penetrate into the pores of a granulated gel, but pass between its particles. Smaller macromolecules penetrate into the gel pores which correspond to their dimensions, and polymer fractionation thus occurs.

A high-molecular fraction remains in the external volume, since it does not penetrate into the gel pores; therefore, large molecules move in a column at a higher rate, and the first to elute is the high-molecular fraction of a polymer and then the fraction in the order of diminishing molecular mass.

Depending on porosity, every gel has its own region of molecular masses which it may separate. Therefore, several columns having gels with different pore dimensions are employed.

Gel-penetrating chromatography is widely used industrially for separating polymers according to molecular mass. This method

has advantages over other fractionation methods, since separation occurs only according to molecular masses, while in other methods based on polymer solubility, separation may simultaneously occur according to the chemical composition (if a polymer is heterogeneous by its chemical composition). This method is very effective for separating oligomers. It may be used to separate dimers, trimers, tetramers, and so forth.

Analytical fractionation methods include ultracentrifugation (p. 505) and turbidimetric titration. The turbidimetric method consists in titrating a solution of a heterogeneous polymer with a

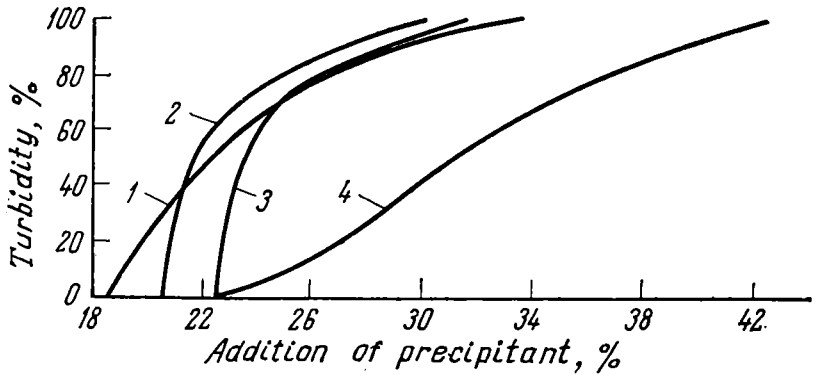


Fig. 12.11. Turbidimetric titration of polystyrenes A and B and their fractions: *1*—polystyrene A; $[\eta]=2.18$; *2*—polystyrene B fraction; $[\eta]=1.99$; *3*—polystyrene B fraction $[\eta]=1.27$; *4*—polystyrene B; $[\eta]=0.64$

precipitant in a special apparatus called a turbidimeter and recording the turbidity of the system. Solution and precipitant must be kept at the same temperature. The increase in turbidity with addition of precipitant can be described by a turbidimetric curve (Fig. 12.11). Such curves are very convenient for a qualitative estimate of the breadth of the molecular-mass distribution of a polymer, i.e., of its polydispersity. Steeply rising curves are characteristic of polymers with narrow molecular-mass distribution. Sloping curves are evidence of high polydispersity of the sample. On the basis of the data obtained the mass of precipitated polymer and its molecular mass can be calculated and its molecular-mass distribution curve plotted (p. 511). Quantitative results obtained by this method are, however, unreliable and it is used mainly for qualitative investigation of polydispersity of polymers.

12.6. RESISTANCE OF POLYMERIC MATERIALS TO SOLVENTS

It is very important that polymeric materials should not interact with the medium during service. Evidently, this can be achieved by using strongly polar polymers in nonpolar media, or nonpolar polymers in polar media. Thus, the most resistant to wa-

ter or water vapours are polyethylene, polypropylene, polybutadiene, polytetrafluoroethylene, polystyrene, poly(vinyl chloride), and organosilicon polymers. All the polymers indicated are hydrophobic and do not swell in water. On the other hand, polymers containing hydroxyl groups are hydrophilic and nonresistant to water.

Nonpolar polymers are not resistant to mineral oils and gasoline, which consist mainly of saturated hydrocarbons. They swell in these media even if they have a spatial network. That is why natural rubber, synthetic polyisoprene, polybutadiene, and butadiene-styrene rubber resist oils and gasoline poorly.

Articles made of these polymers cannot be used in oils or gasoline. Evidently for this purpose rubbers (and polymers) containing polar groups should be used. Some oil- and gasoline-resistant rubbers are polychloroprene and nitrile rubbers. The resistance of the latter to oils increases with increasing content of nitrile groups. Poly(vinyl alcohol) and polytetrafluoroethylene are highly resistant to oils and gasoline and do not dissolve or swell in any known solvent.

Another very important characteristic of polymers, in addition to water and gasoline resistance, is their stability to attack by various aggressive media, such as concentrated acids (nitric or sulphuric). The most resistant in this respect are poly(vinyl chloride) and especially polytetrafluoroethylene.

However, high resistance to solvents is very often combined in polymers with low values of other characteristics. For example, improving oil and gasoline resistance by increasing the number of polar groups (CN) in the chain lowers the frost resistance of the polymer (Chap. 8). But industry requires polymers combining high frost and oil resistance. One of the ways of obtaining polymers possessing properties characteristic of entirely different types of macromolecular compounds is by producing graft copolymers (Chap. 2). For example, by grafting a frost-resistant polymer onto the chain of an oil-resistant polymer, the properties of both polymers can be preserved.

This chapter has described only the general ideas of the solution and swelling of polymers. Since these processes are of great practical importance, the theory of solutions of macromolecular compounds requires elaboration. Definite progress has been made in recent years, and these questions will be discussed in greater detail in the following chapters.

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CHAPTER 13

Thermodynamics of Polymer Solutions

Like any other system, a solution is characterized by the following thermodynamic parameters: volume V, internal energy U, entropy S, Gibbs free energy G *, enthalpy H, etc.

However, one usually makes use of the differences of these quantities in two specified states of the system: $\Delta G = G_2 - G_1$; $\Delta H = H_2 - H_1$, etc.

In the case of solution processes it is customary to determine the difference between the thermodynamic functions of the solution and the same functions of the components before dissolving:

$$\begin{aligned} \Delta G &= G_{\text{sol}} - \sum G_{\text{comp}} \quad \text{free energy of mixing} \\ \Delta H &= H_{\text{sol}} - \sum H_{\text{comp}} \quad \text{enthalpy of mixing} \\ \Delta S &= S_{\text{sol}} - \sum S_{\text{comp}} \quad \text{entropy of mixing} \end{aligned} \tag{13.1}$$

If the thermodynamic quantity characterizing the state of the solution equals the sum of thermodynamic quantities of its components, it is an additive quantity, e.g.,

$$Z_{\text{sol}} = N_1 Z_1^0 + N_2 Z_2^0 + N_3 Z_3^0 + \ldots \tag{13.2}$$

where Z_1^0, Z_2^0, and Z_3^0 = values of molar thermodynamic functions of pure components

N_1, N_2, and N_3 = their mole fractions in the solution.

The properties of real solutions are nonadditive:

$$V_{\text{sol}} \neq \sum V_{\text{comp}}; \quad H_{\text{sol}} \neq \sum H_{\text{comp}}, \text{ etc.}$$

Hence, the volume, enthalpy, entropy, etc., of components in solution differ from their values before dissolving. This made it nec-

* Also called free energy at constant pressure.

essary to introduce the concept of partial molar (specific) functions to characterize the thermodynamic behaviour of components in a solution.

13.1. PARTIAL MOLAR (SPECIFIC) FUNCTIONS. METHODS OF CALCULATING PARTIAL FUNCTIONS

One of the most important functions characterizing the behaviour of each component in a solution is the chemical potential of the component μ_i. According to Gibbs, the chemical potential equals the change in internal energy of a solution on addition of an infinitely small number of moles of the ith component, referred to that amount of substance at constant volume, entropy, and quantity of each of the other components:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{V, S, n_j (j \neq i)} \tag{13.3}$$

It can be shown that if the other parameters are kept constant, the chemical potential is equal to the derivatives of the thermodynamic potentials G, H, or F with respect to n_i:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{V, S, n_j} = \left(\frac{\partial G}{\partial n_i}\right)_{p, T, n_j} = \left(\frac{\partial H}{\partial n_i}\right)_{p, S, n_j} = \left(\frac{\partial F}{\partial n_i}\right)_{V, T, n_j} \tag{13.4}$$

Thus, the chemical potentials at different constant parameters are determined by the change in different thermodynamic potentials.

Lewis suggested a method of calculating the changes in all the thermodynamic potentials at constant pressure and temperature. At p, T = const the addition of an infinitely small amount of the component i to the solution changes its enthalpy, entropy, and Gibbs free energy. These infinitely small changes referred to 1 mole of the component added, i.e., divided by the quantity dn_i, are called the *partial molar enthalpy* H_i, *entropy* S_i, and *Gibbs free energy* G_i:

$$H_i = \left(\frac{\partial H}{\partial n_i}\right)_{p, T, n_j}; \quad S_i = \left(\frac{\partial S}{\partial n_i}\right)_{p, T, n_j}; \tag{13.4a}$$

$$G_i = \left(\frac{\partial G}{\partial n_i}\right)_{p, T, n_j}$$

This involves a change in the volume of the solution of dV. The derivative $\left(\frac{\partial V}{\partial n_i}\right)_{p, T, n_j} = V_i$ is the partial molar volume of component i in the solution.

It follows from comparison of Eqs. (13.4) and (13.4a) that the partial molar Gibbs free energy coincides with the chemical potential:

$$G_i = \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{p,\ T,\ n_j\ (j \neq i)} \tag{13.5}$$

Denoting by Z any *extensive* thermodynamic function * (G, F, H, U, V, etc.), any partial molar function can be written in the general form:

$$Z_i = \left(\frac{\partial Z}{\partial n_i}\right)_{p,\ T,\ n_j\ (j \neq i)} \tag{13.6}$$

The quantities of interest in considering processes of solution are the differences between the partial molar thermodynamic functions of the components in solution (V_i, S_i, H_i, etc.) and their values for the same components prior to dilution (V_i^0, S_i^0, H_i^0, etc.):

$$V_i - V_i^0 = \Delta V_i; \quad H_i - H_i^0 = \Delta H_i;$$
$$S_i - S_i^0 = \Delta S_i; \quad G_i - G_i^0 = \Delta G_i = \Delta \mu_i$$

All known thermodynamic relations are valid for the partial molar functions, e.g.,

$$G_i = H_i - TS_i \tag{13.7}$$

$$\Delta\mu_i \equiv \Delta G_i = \Delta H_i - T\Delta S_i \tag{13.8}$$

Partial molar functions are related by the expression

$$Z = Z_1 n_1 + Z_2 n_2 + Z_3 n_3 + \ldots \tag{13.9}$$

where Z = extensive thermodynamic function of the system
Z_1, Z_2, Z_3, etc. = corresponding partial molar functions
n_1, n_2, n_3, etc. = numbers of moles of the components.

The number of moles of each component contained in one mole of solution is its molar fraction; then Eq. (13.9) may be written as follows:

$$Z = Z_1 N_1 + Z_2 N_2 + Z_3 N_3 + \ldots \tag{13.10}$$

For one mole of a binary solution,

$$V = V_1 N_1 + V_2 N_2; \quad S = S_1 N_1 + S_2 N_2$$
$$H = H_1 N_1 + H_2 N_2; \quad G = G_1 N_1 + G_2 N_2 \tag{13.11}$$

Equations (13.11) are also valid for increments of thermodynamic functions:

$$\Delta V = \Delta V_1 N_1 + \Delta V_2 N_2; \quad \Delta S = \Delta S_1 N_1 + \Delta S_2 N_2$$
$$\Delta H = \Delta H_1 N_1 + \Delta H_2 N_2; \quad \Delta G = \Delta G_1 N_1 + \Delta G_2 N_2 \tag{13.12}$$

* An extensive thermodynamic function is a function depending on the mass of the components of the system.

Knowing the difference of partial molar functions of the components and the composition of the solution, one can calculate the total difference of the extensive function from Eq. (13.12).

The change in partial molar functions is expressed by the equation

$$N_1 dZ_1 + N_2 dZ_2 + N_3 dZ_3 + \ldots = 0 \tag{13.13}$$

For a binary solution

$$N_1 dZ_1 + N_2 dZ_2 = 0 \tag{13.14}$$

Dividing Eq. (13.14) by dN_1, we get

$$N_1 \frac{dZ_1}{dN_1} + N_2 \frac{dZ_2}{dN_1} = 0 \tag{13.15}$$

whence

$$N_1 \frac{dZ_1}{dN_1} = -N_2 \frac{dZ_2}{dN_1} \tag{13.16}$$

Since in a binary solution $N_1 + N_2 = 1$ or $dN_1 = -dN_2$, Eq. (13.16) can be written as follows:

$$N_1 \frac{dZ_1}{dN_1} = N_2 \frac{dZ_2}{dN_2} \tag{13.17}$$

In this form the equation is often called the Gibbs-Duhem equation. It is also valid for ΔZ_1:

$$N_1 \frac{d(\Delta Z_1)}{dN_1} = N_2 \frac{d(\Delta Z_2)}{dN_2} \tag{13.18}$$

Knowing the change in a partial molar function of one component depending on composition, the change in the partial molar function of the other component depending on composition can be calculated from Eqs. (13.17) and (13.18). To do so one integrates Eq. (13.18) within definite limits:

$$N_2 d(\Delta Z_2) = -N_1 d(\Delta Z_1) \tag{13.19}$$

$$\int d(\Delta Z_2) = -\int_a^b \frac{N_1}{N_2} d(\Delta Z_1) \tag{13.20}$$

or

$$\Delta Z_2 = -\int_a^b \frac{N_1}{N_2} d(\Delta Z_1) \tag{13.21}$$

where a and b are the values of ΔZ_1 corresponding to two definite concentrations of the solution, i.e., to two values of the ratio $\frac{N_1}{N_2}$.

If the molecular masses of the components are not known exactly, so that their mole fractions cannot be calculated, it is more convenient to use specific partial functions, i.e., functions referred to 1 g, rather than to 1 mole of the component.

A partial specific function equals the partial molar function divided by the molecular mass of the component:

$$Z_{i_{sp}} = \frac{Z_{i_{mol}}}{M_i} \tag{13.22}$$

All the thermodynamic relations given above are valid for specific partial functions.

There are two graphical methods for calculating partial functions.

The first method, known as the *tangent method*, consists in plotting the dependence of some thermodynamic function (Z_{tot}), say, the volume of solution V, on the number of moles of one of its components (Fig. 13.1).

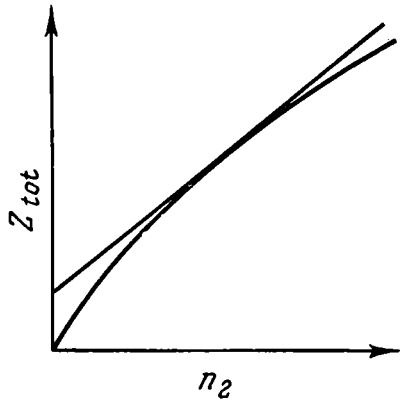

Fig. 13.1. Determining partial molar or specific thermodynamic quantities (tangent method)

Evidently, the derivative $\partial V/\partial n_2$, determined at any point of the curve, equals the partial molar volume V_2 of the component in a solution of the corresponding concentration.

The disadvantage of this method is that it enables calculation of partial functions for only one component.

The second method, known as the *intercept method*, consists in plotting the value of some thermodynamic function of the solution (Z_{tot}) or its change (ΔZ_{tot}) referred to 1 mole of solution [e.g., $V_{tot}/(n_1 + n_2)$ or the integral heat of solution $\Delta H_{tot}/(n_1 + n_2)$] as the ordinates against the composition of solution in mole fractions (Fig. 13.2). These quantities are known as the average enthalpy of mixing h, and the average volume of mixing v. One may also speak of the average entropy of mixing $s = S/(n_1 + n_2)$, of the average free energy of mixing $g = G/(n_1 + n_2)$, etc. If a tangent to the curve is drawn through any of its points, the intercepts on the ordinate axis will equal the partial molar functions (V_1 and V_2 or ΔH_1 and ΔH_2). If general thermodynamic functions referred to 1 g of solution [$V_{tot}/(g_1+g_2)$] are plotted along the ordinate axis against composition in weight fractions, the tangent intercepts on the ordinate will be numerically equal to the partial specific functions.

Partial molar functions depend on the composition of the solution. This dependence [see Eq. (13.17)] may be written in the following form:

$$\frac{\partial Z_1/\partial N_1}{\partial Z_2/\partial N_2} = \frac{N_2}{N_1} \tag{13.23}$$

Suppose the solution is infinitely dilute with respect to the second component ($N_2 \to 0$; $N_1 \to 1$). Then $N_2/N_1 \to 0$ and hence

$$\frac{\partial Z_1/\partial N_1}{\partial Z_2/\partial N_2} \to 0 \qquad (13.24)$$

Equation (13.24) has two solutions:

$$\begin{aligned} &(1)\ \lim \frac{\partial Z_1}{\partial N_1} = 0 && \lim \frac{\partial Z_2}{\partial N_2} \neq 0 \\ &(2)\ \lim \frac{\partial Z_1}{\partial N_1} \neq 0 && \lim \frac{\partial Z_2}{\partial N_2} = \infty \end{aligned} \qquad (13.25)$$

According to solution (1) the partial enthalpies and volumes, and according to solution (2) the partial entropies and Gibbs free energies of the components vary with composition.

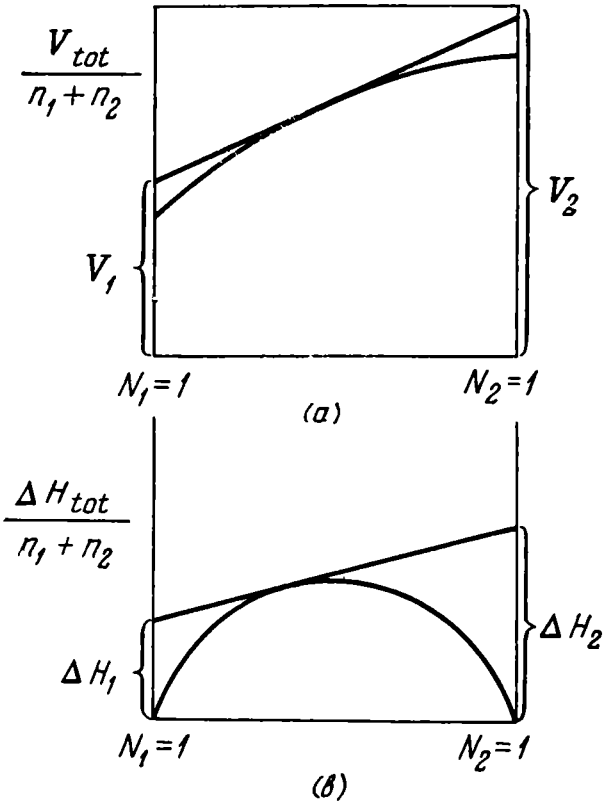

Fig. 13.2. Determining partial molar thermodynamic quantities (intercept method):
a—partial molar volumes; *b*—partial molar enthalpies

Solution (1) signifies that at $N_1 = 1 (N_2 = 0)$ the abscissa touches the curve $\Delta H_1 = f(N_1)$ or $\Delta V_1 = f(N_1)$, and the slope of these curves to the abscissa axis at $N_2 = 1 (N_1 = 0)$ is a finite value. With $N_2 = 1 (N_1 = 0)$ the abscissa touches the curve

$\Delta H_2 = f(N_1)$ or $\Delta V_2 = f(N_1)$, and the slope of these curves to the abscissa axis at $N_1 = 1$ ($N_2 = 0$) is a finite value (Fig. 13.3*a*).

The second solution signifies that at $N_1 = 1$ ($N_2 = 0$) the angle of slope of the curve $\Delta G_1 = f(N_1)$ is acute and the curve $\Delta G_2 = f(N_2)$ tends to minus infinity. At $N_2 = 1$ ($N_1 = 0$) the angle of

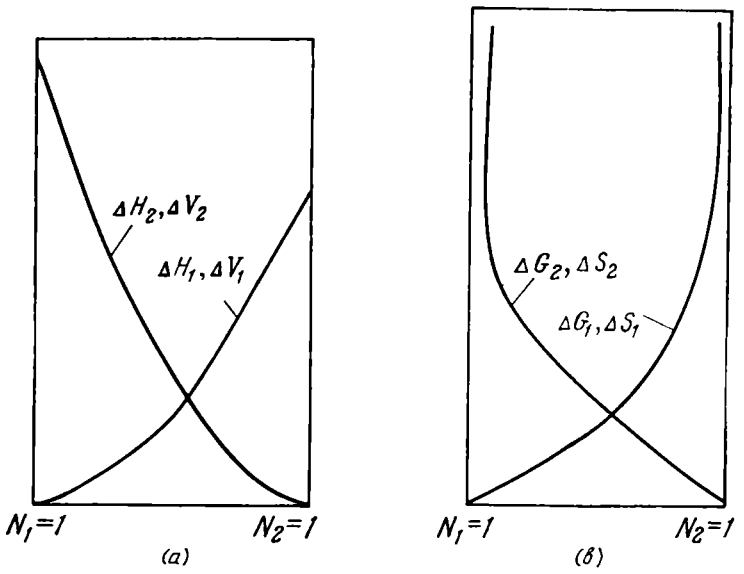

Fig. 13.3. Variation of partial molar quantities with composition: *a*—variation of ΔH_i and ΔV_i; *b*—variation of ΔG_i and ΔS_i

slope of the curve $\Delta G_2 = f(N_2)$ is acute, and the curve $\Delta G_1 = f(N_1)$ tends to minus infinity (Fig. 13.3*b*). From the equation $\Delta G_i = RT \ln p_i/p_i^0$ it follows that ΔG_i varies depending on composition. At $N_i = 1$ the ratio $p_i/p_i^0 = 1$, and hence $\Delta G_i = 0$. If $N_i = 0$, then $p_i = 0$, and hence $\Delta G_i = -\infty$.

At $N_i = 1$ the value of $\Delta S_i = -R \ln N_i = 0$; at $N_i = 0$, $\Delta S_i = +\infty$.

Thus, ΔG_i varies with the composition of solution from zero to minus infinity, and ΔS_i, from zero to infinity.

13.2. IDEAL AND NONIDEAL SOLUTIONS

Ideal solutions are those which form with a zero heat effect $\Delta H_i = 0$, $\Delta H = 0$ and an ideal entropy of mixing * $\Delta S_i \equiv \Delta S_{i_{id}} = -R \ln N_i$. Consequently, in accordance with Eq. (13.8) the change in chemical potential of the *i*th component in an ideal solution equals

$$\Delta\mu_i = -T\Delta S_{i_{id}} = RT \ln N_i \qquad (13.26)$$

* For more details on the ideal entropy of mixing see p. 398.

i.e., depends only on the mole fraction of that component in the solution.

In the case of a real solution,

$$\Delta\mu_i = \Delta G_i = RT \ln \frac{p_i}{p_i^0} \qquad (13.27)$$

where p_i and p_i^0 are the partial vapour pressures of the ith component above the solution and above the pure component, respectively.

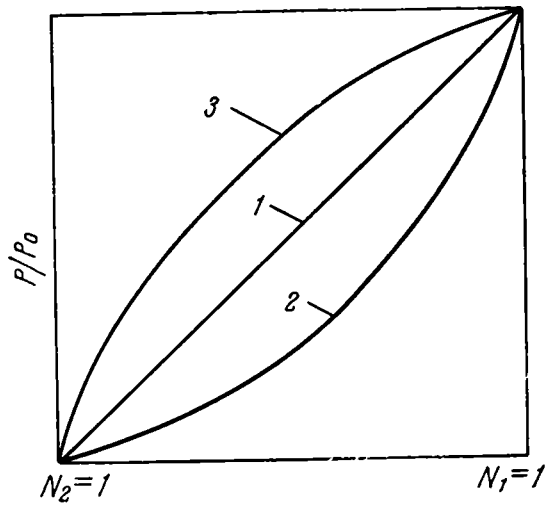

Fig. 13.4. Dependence of vapour pressure on composition of solution:

1—ideal solution $p_1/p_1^0 = N_1$; *2*—negative deviations from ideality $p_1/p_1^0 < N_1$; *3*—positive deviation from ideality $p_1/p_1^0 > N_1$

Replacing vapour pressure ratio by fugacity * ratio, one may write

$$\Delta\mu_i = RT \ln \frac{f_i}{f_i^0} \qquad (13.28)$$

where f_i and f_i^0 are the fugacities of the component above the solution and above the pure component, respectively. Comparing Eqs. (13.26) and (13.27), we obtain

$$\frac{p_i}{p_i^0} = N_i \qquad (13.29)$$

Expression (13.29) was obtained empirically by Raoult and is called Raoult's law. Hence, in ideal solutions Raoult's law holds over the entire range of compositions, this being represented graphically by a straight line (Fig. 13.4).

Ideal solutions usually form when substances of similar chemical structure and molecular size are mixed. In this case the energies of interaction between like and unlike molecules are close and the entropy of mixing is at its ideal value. The formation of ideal solutions involves no change in volume ($\Delta V = 0$, i.e., $V_i = V_i^0$).

It follows from the above that on formation of an ideal solution the enthalpy and volume of the solution are the sums of the enthalpies and volumes of individual components ($\Delta H_i = 0$ and $\Delta V_i = 0$). As to the entropy and Gibbs free energy, their changes are

* *Fugacity* is a function of pressure, temperature, and concentration, used instead of partial pressures for solving thermodynamic equations for real gases.

not additive even in an ideal solution:

$$G_{sol} \neq \sum G_i^0 n_i \quad S_{sol} \neq \sum S_{comp}$$
$$\Delta G_i \equiv \Delta\mu_i = RT \ln N_i \quad \Delta S_i = -R \ln N_i$$

In reality most solutions do not obey Eqs. (13.26) and (13.29). Such solutions are called *nonideal*, or *real*. In them the partial vapour pressure of the dissolved component over the solution also decreases with increasing concentration; however, in this case both positive $(p_1/p_1^0 > N_1)$ and negative $(p_1/p_1^0 < N_1)$ deviations from ideality are observed (see Fig. 13.4).

Negative deviations from ideality are evidence of a decrease in the number of molecules of the given component in the vapour phase, i.e., of good interaction between the components in solution. Positive deviations from ideality are due to poor interaction between the components, as a result of which the molecules tend to pass into the vapour phase in larger amounts, increasing the partial vapour pressure p_i.

It follows from Eq. (13.26) that deviations from ideality in solutions result from violation of the following conditions:

$$\Delta H \neq 0 \text{ and } \Delta H_i \neq 0$$
$$\Delta S_{mix} \neq \Delta S_{mix_{id}} \qquad (13.30)$$

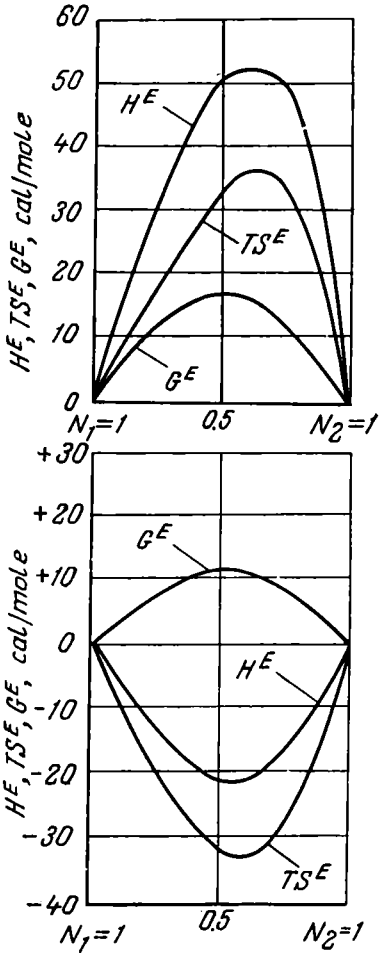

Fig. 13.5. Variation of an excess thermodynamic function with composition

Two methods are commonly used to estimate the degree of deviation from ideality.

The first method, due to Scatchard, consists in calculating the so-called *excess change of thermodynamic function*, this being the difference between the change of the function on the formation of the real solution in question and its change on formation of an ideal mixture.

Denoting the changes in the Gibbs free energy, enthalpy, and entropy involved in the formation of the nonideal solution by G^M, H^M, and S^M ($G^M = \Delta G$; $H^M = \Delta H$; $S^M = \Delta S$) and the changes of the same functions on formation of an ideal solution by G^I, H^I, and S^I, the excess function can be written as the difference of

these values:

$$G^E = G^M - G^I \tag{13.31}$$

$$S^E = S^M - S^I \tag{13.32}$$

Since upon formation of an ideal solution $H^I = \Delta H = 0$,

$$H^E = H^M \tag{13.33}$$

When liquids are mixed, the excess of thermodynamic function may be positive or negative; e.g., the excess of enthalpy may be positive or negative, which corresponds to endothermal and exothermal solution, respectively. The excess of entropy may also be positive or negative.

Figure 13.5 shows experimental curves of the dependence of the excess of thermodynamic functions on composition for mixtures of aliphatic and alicyclic hydrocarbons. The upper set of curves shows that the excess of all the thermodynamic functions is positive in the case considered. The lower set of curves shows that a positive excess of Gibbs free energy may correspond to a negative excess of entropy and enthalpy.

The second method of estimating the deviation of solutions from ideality, suggested by Lewis, consists in substituting a certain function called *activity* for the mole fractions in all thermodynamic equations which are not valid for real solutions. Thus, instead of Eqs. (13.26) and (13.29) we may write

$$\Delta\mu_i = RT \ln a_i \tag{13.34}$$

$$\frac{p_i}{p_i^0} = a_i \tag{13.35}$$

Knowing the values of p_i/p_i^0 or $\Delta\mu_i$ the activity value can be calculated from either of these equations. The deviation of this value from the concentration of a given component in the solution is a measure of deviation from ideality.

13.3. THERMODYNAMIC AFFINITY OF A SOLVENT TO A POLYMER OR THERMODYNAMIC QUALITY OF A SOLVENT

The first question that a researcher in the problem of solution asks himself is whether substances are capable of intermixing or interdissolving. Thermodynamically, this implies whether a process would occur spontaneously in the direction of mixing the components together or not. Is there an affinity between them?

Processes at constant pressure and temperature (dilution usually takes place under these conditions) occur spontaneously in the direction of a diminution in the Gibbs free energy G or in the direction of a diminution in the chemical potential of every compo-

nent μ_i, i.e., the final state of a system should have smaller values of these parameters than the initial one. It follows that a solution should have less free energy than the sum of free energies of the components:

$$G_{sol} < \sum G_i^0 n_i \tag{13.36}$$

where G_i^0 = free energy of one mole
n_i = number of moles of the ith component.

The chemical potential of a component in a solution should be less than the chemical potential of the same component prior to dissolution:

$$\mu_i < \mu_i^0$$

and their differences should be negative:

$$\Delta G_{sol} \equiv G_{sol} - \sum G_i^0 n_i < 0; \quad \Delta\mu_i < 0 \tag{13.37}$$

The difference between the free energy of a solution and that of the components is known as the *free energy of mixing* ΔG^m. Hence,

$$\Delta G^m < 0 \quad \Delta\mu_i < 0 \tag{13.38}$$

The process occurs in the direction of a combination of the components only if there is affinity between them. Therefore, the criteria of affinity and direction are the same ($\Delta G < 0$; $\Delta\mu_i < 0$). The higher is the absolute value of these differences, the greater is the *thermodynamic affinity* between the components and the more perfect is the process of their interaction.

Solvents are classified into good and poor ones by the extent of thermodynamic affinity, i.e., the *thermodynamic quality* of a solvent is assessed. Thermodynamically *good* solvents are those with high absolute values of the quantities ΔG and $\Delta\mu_i$ when they interact with polymers. *Poor* solvents are those whose interaction with polymers is accompanied with a small change in free energy or chemical potential. Hence, it is necessary to know the values of ΔG and $\Delta\mu_i$ in order to estimate the quality of a solvent. This determination may be made by ascertaining solvent vapour pressure over a solution, measuring the osmotic pressure of a solution or swelling pressure, and also by determining the so-called second Virial coefficient.

13.4. VAPOUR PRESSURE OVER POLYMER SOLUTIONS

In a state of equilibrium there are always vapours of the components above a liquid solution.

A macromolecular compound cannot practically be transferred to the vapour state, and hence the partial pressure of its vapour over the solution $p_2 \approx 0$. Therefore the vapour pressure usually

measured over polymer solutions is essentially the vapour pressure of the low-molecular component, which is always smaller than the vapour pressure over the pure solvent. The higher the concentration of a polymer, the smaller the value of p_1, and the more it differs from the vapour pressure over the pure low-molecular component p_1^0. The most substantial difference between p_1 and p_1^0 is observed at high concentrations of a polymer in the solution. In

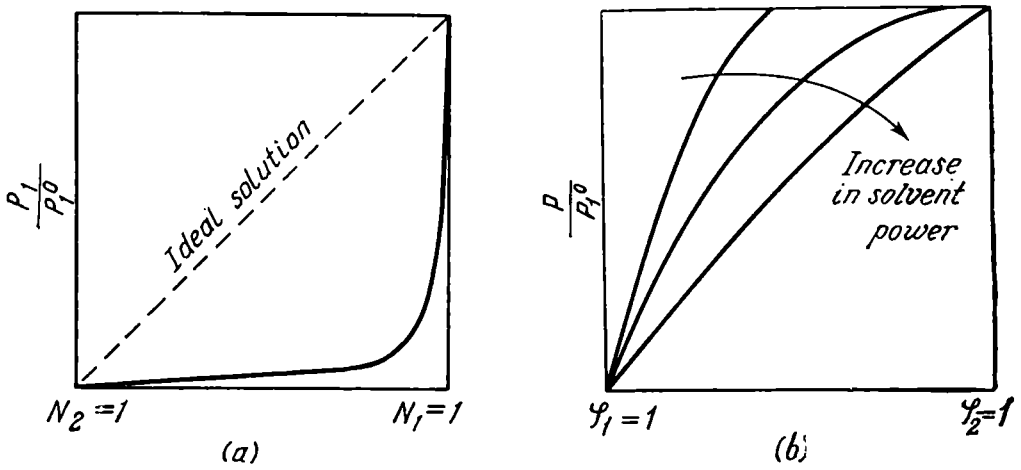

Fig. 13.6. Dependence of vapour pressure over a polymer solution on mole fraction of components (*a*) and dependence of vapour pressure over polystyrene solution on weight fraction of components (*b*)

dilute solution (ω_2 being small) the difference between these values is so insignificant that very precise and sensitive methods are required to measure p_1.

Vapour pressures are measured either over solutions prepared beforehand or over solutions formed by the polymer absorbing solvent vapour.

Polymer solutions characteristically display sharp negative deviations from ideality, as can be seen clearly in Fig. 13.6*a*, which shows the dependence of the relative vapour pressure over the solution on the mole fraction of a polymer in the solution. The curves in Fig. 13.6*b* are typical dependencies of relative vapour pressure over a polymer solution on composition in weight or volume fractions.

Since for a thermodynamically stable solution $p_i < p_i^0$, according to Eq. (13.27), $\Delta\mu_i < 0$, i.e., the chemical potential of each component in the solution is smaller than that of the pure component:

$$\mu_i < \mu_i^0 \tag{13.39}$$

Thus, dissolution is a spontaneous process. As more and more of component i passes into the phase with the lower chemical poten-

tial, the value of the latter in that phase increases, and hence $\partial\mu_i/\partial c_i$ is substantially positive. The value of μ_1 increases until $\mu_1 = \mu_1^0$ ($\Delta\mu_i = 0$), which corresponds to equilibrium. In the case of complete miscibility of the polymer with the low-molecular liquid, this occurs when all of the solvent has passed into solution, i.e., when $\varphi_1 = 1$. In the case of limited swelling of the polymer the value of $\Delta\mu_1$ becomes zero at a certain value of φ_1, corresponding to the maximum degree of swelling.

13.5. OSMOTIC PRESSURE

Osmosis is the phenomenon of penetration of a solvent into a solution through a semipermeable membrane, i.e., through a membrane that is permeable to solvent molecules but impermeable to solute molecules, in particular, to large polymer molecules.

The tendency of solvent molecules to pass spontaneously into a solution, due to the inequality $\mu_1 < \mu_1^0$, is estimated quantitatively by *osmotic pressure*. The latter actually has the dimension of pressure (atm). But it differs substantially in nature from gas pressure, i.e., it is not the result of molecular impacts on the walls of a vessel or a semipermeable membrane. The osmotic pressure of a solution is the thermodynamic affinity between its components referred to unit volume of the solvent: $\pi = \frac{\Delta\mu_1}{V_1}$. This is shown below.

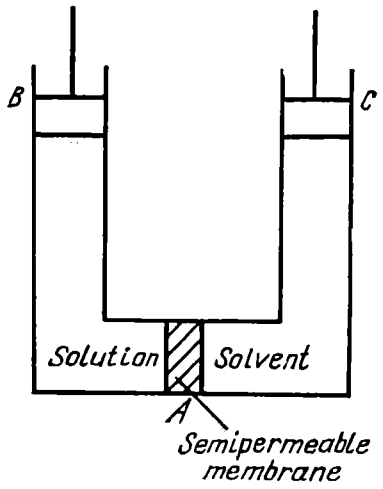

Fig. 13.7. Equilibrium between osmotic and external pressures

Suppose the volume AC (Fig. 13.7) contains a pure solvent, and the volume AB, a solution of some component in the solvent. The volumes are separated by a membrane permeable only to solvent. If the external pressure on both pistons is the same, the solvent will pass from volume AC to volume AB and piston B will rise.

If the pressure on piston B is increased to offset the tendency of solvent to pass into solution, dynamic equilibrium will be established in the system, under which $\mu_1 = \mu_1^0$. Let p^0 denote the external pressure on the pure solvent, and p, the pressure on the solution. At the moment of equilibrium the excess pressure $p - p^0$ becomes equal to the osmotic pressure π:

$$\pi = p - p^0 \tag{13.40}$$

Thus, the *osmotic pressure of a solution* is equal to the additional pressure which must be applied to the solution to make the

chemical potential of the component in solution equal to the chemical potential of the pure solvent.

The change in chemical potential of solvent with environmental pressure at constant temperature is given by the equation

$$\left(\frac{\partial \mu_i}{\partial p}\right)_T = V_1$$

or

$$d\mu_i = V_1 dp \tag{13.41}$$

Hence,

$$\int_{\mu_1}^{\mu_1^0} d\mu_i = \int_{p^0}^{p} V_1 \, dp$$

Assuming V_1 to be constant, we obtain after integration

$$\mu_1^0 - \mu_1 = V_1 (p - p^0) = V_1 \pi \tag{13.42}$$

where π = osmotic pressure

V_1 = partial molar volume of solvent.

Hence,

$$\mu_1 - \mu_1^0 = \Delta\mu_1 = -V_1 \pi \tag{13.43}$$

Equation (13.43) is valid only if the solution is noncompressible ($V_1 = \text{const}$).

Knowing V_1 and measuring the osmotic pressure, the value of $\Delta\mu_1$ can be calculated from Eq. (13.43).

Osmotic pressures are measured with instruments called *osmometers*. They are vessels in which an osmotic cell filled with the polymer solution communicates with a narrow capillary. The solution rises up the capillary until the osmotic pressure is balanced by the weight of the hydrostatic column formed. The viscosity of the solution rises considerably with increasing concentration of a polymer, making it difficult for the solution to ascend the osmometer capillary. For this reason osmotic pressure measurements are usually restricted to very dilute solutions ($c < 1$ g/100 ml). There are very few studies in which the osmotic pressure of solutions was determined in the range of higher concentrations.

13.6. SWELLING PRESSURE

Solutions with high concentrations of a polymer are essentially solutions of the low-molecular component in the polymer, or swollen polymer. Swelling of a polymer can be accomplished without increase of volume (by confining the sample in rigid walls on all sides and leaving only a hole for adding the solvent). The swollen sample will then exert a pressure on its confining walls, called the *swelling pressure.*

Swelling pressure and osmotic pressure are phenomena of the same nature. Both result from interaction of the low-molecular component with a polymer. Upon limited swelling or during the first stage of unlimited swelling the polymer simultaneously plays the part of the semipermeable membrane and the osmotic cell containing the solution. The molecules of the low-molecular component penetrate into this solution whereas the polymer molecules cannot pass from the solution into the solvent. In dilute solutions one measures the osmotic pressure π; in more concentrated solutions one measures the swelling pressure p. If the values of π and π_{swel} are plotted against polymer concentration in solution, the π vs. c curve should pass smoothly into the π_{swel} vs. c. Knowing the swelling pressure p and substituting it into Eq. (13.43), one can calculate the value of $\Delta\mu_1$ for the region of very concentrated solutions:

$$\Delta\mu_1 = -\pi_{swel} V_1 \tag{13.44}$$

The first works on the measurement of swelling pressure were written by Poznyak, who studied the swelling of unvulcanized rubber in different organic liquids and gelatin in water. He derived the equation

$$\pi_{swel} = \pi_0 c^k \tag{13.45}$$

where c = polymer concentration
π_0 and k = empirical constants.

The investigation was conducted in a narrow concentration region, and the values of swelling pressure were within 0.8-6 atm. In reality, swelling pressure may attain hundreds of atmospheres (p. 364).

By combining Eqs. (13.43) and (13.27), we obtain the expression

$$\pi = -\frac{RT}{V} \ln \frac{p_i}{p_i^0} \tag{13.46}$$

which makes it possible to calculate the osmotic pressure of a solution or swelling pressure on the basis of the measured values p_i/p_i^0. This is especially fruitful when studying the interaction of spatially crosslinked polymers with solvents.

13.7. SECOND VIRIAL COEFFICIENT

A comparison of Eqs. (13.43) and (13.26) shows that the osmotic pressure of an ideal solution can be given by the relation

$$\pi = -\frac{RT}{V_1^0} \ln N_1 \tag{13.47}$$

Expanding $\ln(1 - N_2)$ in a series, and using the first term of this series for high dilutions, we obtain

$$\ln N_1 = \ln(1 - N_2) = -N_2 - \frac{N_2^2}{2} - \ldots \tag{13.48}$$

$$\pi = \frac{RT}{V_1^0} N_2 \tag{13.49}$$

The mole fraction of a component is

$$N_2 = \frac{n_2}{n_1 + n_2}$$

where n_1 and n_2 are the numbers of moles of the components. If $n_1 \gg n_2$, then $N_2 \approx n_2/n_1$. Substituting this expression into Eq. (13.49), we get

$$\pi = \frac{RT}{V} n_2 = c_2 RT \tag{13.50}$$

where V = volume of solution, equal to $n_1 V_1^0$

$c_2 = \frac{n_2}{V}$ = concentration of a solute, mole/litre.

Equation (13.50) was first derived empirically by van't Hoff, and is known as the van't Hoff equation.

The van't Hoff equation $\pi = RTc_2$ does not apply to polymer solutions, even though very dilute. The concentration dependence of osmotic pressure is expressed by a more complex equation which results if the concentration c_2 is replaced by a power series:

$$\pi = RT(A_1 c_2 + A_2 c_2^2 + A_3 c_2^3 + \ldots) \tag{13.51}$$

or

$$\frac{\pi}{c_2} = RT(A_1 + A_2 c_2 + A_3 c_2^2 + \ldots) \tag{13.52}$$

where c_2 = concentration of a polymer in a solution, g/ml

A_1, A_2, A_3, etc. = so-called *Virial coefficients*, whose value can be calculated from the experimental dependence $\pi/c_2 = f(c_2)$.

In the general case this dependence is represented by curves concave to the ordinate axis. The first Virial coefficient A_1 is related directly to the molecular mass of a polymer by the relation $A_1 = 1/M$ (p. 491). Hence, Eq. (13.52) may be written in the following form:

$$\frac{\pi}{c_2} = RT\left(\frac{1}{M} + A_2 c_2 + A_3 c_2^2 + \ldots\right) \tag{13.53}$$

For a number of systems the dependence $\pi/c_2 = f(c_2)$ is a straight line in the region of high dilutions, i.e., $A_3 = 0$, and Eq. (13.53) becomes simpler:

$$\frac{\pi}{c_2} = RT\left(\frac{1}{M} + A_2 c_2\right) \tag{13.54}$$

In this case, for solutions of a single polymer fraction in different solvents the dependence $\pi/c_2 = f(c_2)$ is a series of fanning straight lines (Fig. 13.8). The intercept on the ordinate axis equals RT/M and is independent of the nature of a solvent. The second Virial coefficient characterizes the slope of the straight line. Its value depends on the interaction between a polymer and a solvent.

For an ideal solution the π/c_2 vs. c_2 dependence obeys the van't Hoff law, and its graph is a straight line parallel to the abscissa axis (see Fig. 13.8). Hence, the second Virial coefficient $A_2 = 0$. The solvents of such solutions are called *ideal solvents.*

If

$A_2 = 0$ ideal solvent
$A_2 > 0$ good solvent
$A_2 < 0$ poor solvent

The better a solvent, the higher the value of A_2.

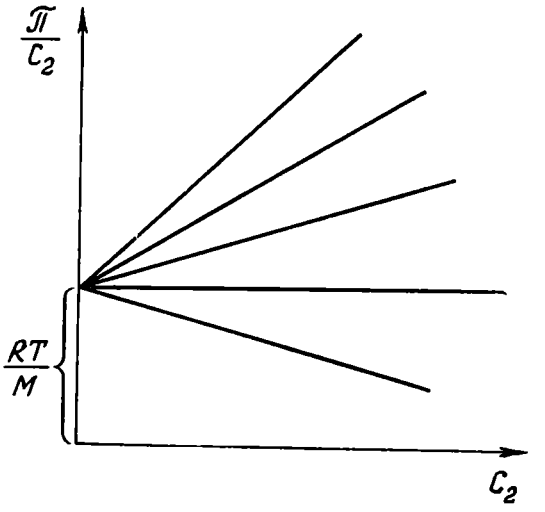

Fig. 13.8. Dependence of π/c_2 on concentration for polymer solutions in various solvents

Table 13.1 gives the second Virial coefficients for several polymer-solvent systems.

TABLE 13.1. *Values of Second Virial Coefficients for Several Polymer-Solvent Systems*

Polymer	$M \times 10^{-3}$	Solvent	Temperature, °C	$A_2 \times 10^{-4}$, cm³·mole/g²
Polystyrene	1600	Toluene	22.0	3.12
	1600	Dichloroethane	22.0	2.88
	1600	Cyclohexane	27.0	—0.37
Polyisobutylene	720	Cyclohexane	30.0	5.38
	720	Benzene	40.0	1.51
Poly(vinyl acetate)	200	Acetone	30.0	6.0
	200	Methyl ethyl ketone	30.0	4.6

13.8. FREE ENERGY OF MIXING OF A POLYMER WITH A SOLVENT

We may calculate only the value of $\Delta\mu_1$ after determining the pressure of solvent vapour over a solution or the osmotic pressure of a solution. To calculate the free energy of mixing ΔG^m, it is

necessary to know also the chemical potential of a polymer or, to be more exact, the quantity $\Delta\mu_2$. Its value is calculated by using the Gibbs-Duhem equation for specific quantities

$$\omega_2 \, d\Delta\mu_2 = -\omega_1 \, d\Delta\mu_1 \tag{13.55}$$

where ω_1 and ω_2 = weight fractions of components.

Hence,

$$\Delta\mu_2 = -\int \frac{\omega_1}{\omega_2} d(\Delta\mu_1) + C \tag{13.56}$$

To solve the equation, it is necessary to plot a graph of dependence of $\frac{\omega_1}{\omega_2}$ on $\Delta\mu_1$ (Fig. 13.9).

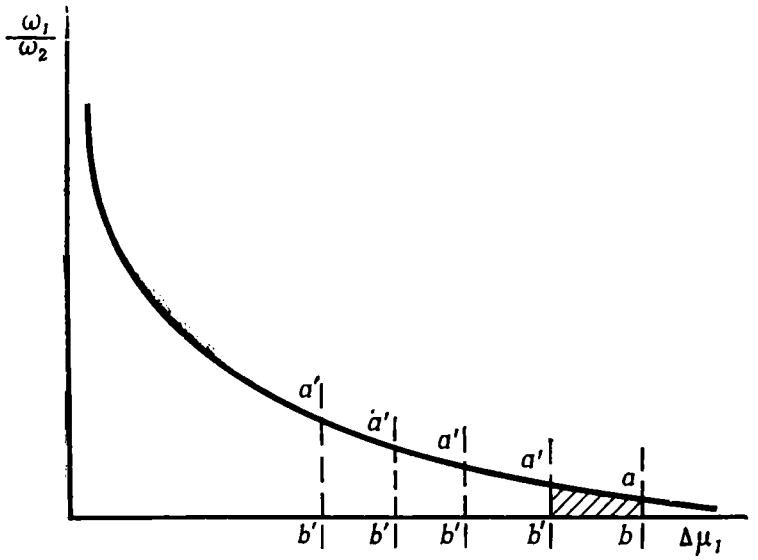

Fig. 13.9. Graph for calculating $\Delta\mu_2$

For $\omega_2 = 1$ $(\omega_1 = 0)$, the ratio $\frac{\omega_1}{\omega_2} = 0$ and $\Delta\mu_1 \to -\infty$.

For $\omega_1 = 1$ $(\omega_2 = 0)$, the ratio $\frac{\omega_1}{\omega_2} = \infty$ and $\Delta\mu_1 = 0$.

Hence, the curve goes with both ends into infinity, and the integral may be determined within the limits ranging from $-\infty$ to a certain value of $\Delta\mu_1$ which corresponds to the concentration of a solution ω_2:

$$\Delta\mu_2 = -\int_{-\infty}^{\Delta\mu_1} \frac{\omega_1}{\omega_2} d(\Delta\mu_1) \tag{13.57}$$

Such an improper integral is replaced with a proper integral which is analogous to it; in this case, the finite value $\Delta\mu_1'$ which conforms to concentration $\omega_2' < 1$ is taken as the lower limit. Thus,

the areas under the curve, that are bounded by ordinates corresponding to $\Delta\mu_1'$ at ω_2' and $\Delta\mu_1$ at different values of ω_2, are calculated. The calculated areas for $\Delta\mu_2'$ are less than the true values of $\Delta\mu_2$, since some part of the area is not taken into account. To obtain the true values of $\Delta\mu_2$, a graph of dependence $\Delta\mu_2 = f(\omega_1)$ is plotted; in the region of concentrations close to $\omega_2 = 1$, it is rectilinear (Fig. 13.10). On extrapolating the straight line to $\omega_2 \to 1$, we obtain segment A. However, at $\omega_2 = 1$, $\Delta\mu_2 = 0$. It follows that the true values of $\Delta\mu_2$ differ from $\Delta\mu_2'$ by the length of segment A.

$$\Delta\mu_2 = \Delta\mu_2' + A \quad (13.58)$$

This is an ordinary way of approximately calculating $\Delta\mu_2$. Knowing $\Delta\mu_1$ and $\Delta\mu_2$, the average free energy of mixing per gram of a solution may be calculated:

$$\Delta G^m = \omega_1 \Delta\mu_1 + \omega_2 \Delta\mu_2 \quad (13.59)$$

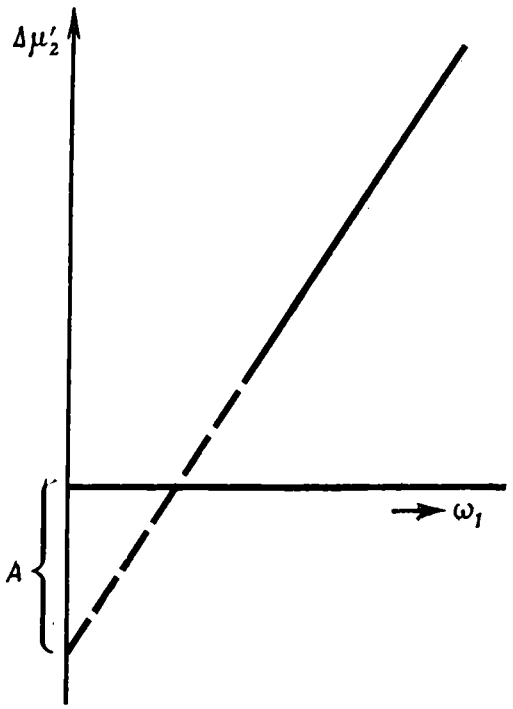

Fig. 13.10. $\Delta\mu_2$ versus ω_1 graph

A typical graph of dependence of the quantities $\Delta\mu_1$, $\Delta\mu_2$ and ΔG^m is given in Fig. 13.11 for the unlimited and limited mixing of a polymer with a solvent. According to the laws of thermodynamics, the quantities $\Delta\mu_1$ and $\Delta\mu_2$ change from values of zero to minus infinity. The curves form finite angles with the abscissa axis. The quantity ΔG^m changes with concentration according to the extreme curve, whose minimum is displaced towards larger concentrations of a polymer. The curves for $\Delta\mu_1$ and $\Delta\mu_2$ intersect at the minimum of curve *3*. The higher is the absolute value of ΔG^m, the better is the solvent.

Hence, *good* solvents are liquids whose mixing with a polymer is accompanied with great changes in the chemical potentials of components and the free energy of the entire system, and with large values of osmotic pressure and swelling pressure and positive values of the second Virial coefficients. *Poor* solvents are liquids which, when mixed with a polymer, experience small changes in the chemical potentials of components and the free energy of a system, and give rise to low osmotic pressures and

swelling pressures and to negative values of the second Virial coefficients.

The quality of a solvent may be determined also by the position of the critical solution temperature on the temperature scale. The

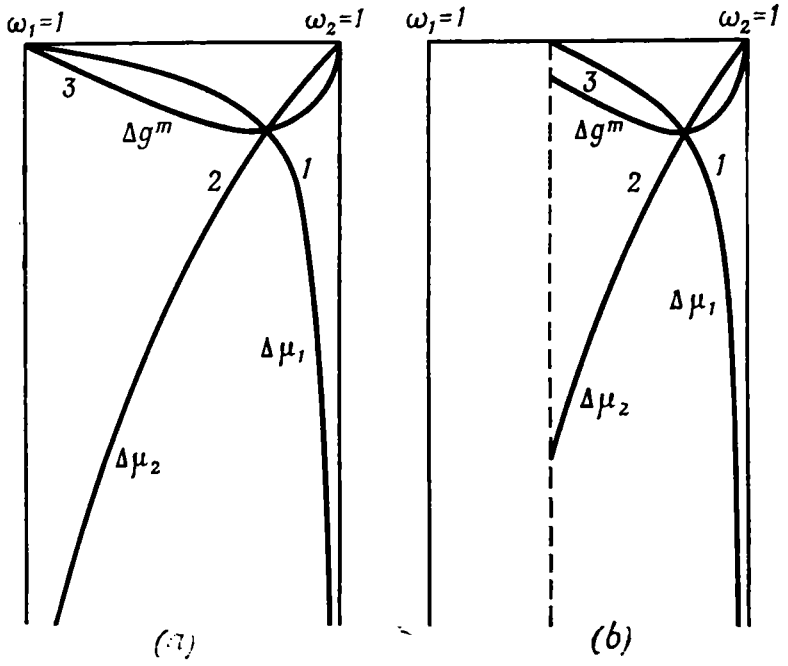

Fig. 13.11. Concentration dependence of the average free energy of mixing ΔG^m and the quantities $\Delta\mu_1$ and $\Delta\mu_2$ for unlimited (*a*) and limited (*b*) polymer mixing

lower is UCST and the higher is LCST, the larger is the region of homogeneous mixing and the better is the solvent for a given polymer.

13.9. THERMODYNAMIC STABILITY OF SYSTEMS

From the standpoint of stability, systems or parts of systems (phases) are classified into stable, unstable and metastable ones.

A *stable* phase is one that is stable in respect of all phases which differ from it in their properties by a finite or an infinitely small quantity.

An *unstable* or a *labile* phase is one that is unstable in respect of all phases which differ from it infinitely little. Therefore, it disappears and a new, more stable phase appears.

A *metastable* phase is one that is stable in respect of all phases which differ from it infinitely little, but there is at least one phase in respect of which it is unstable. A metastable phase remains indefinitely long in equilibrium, and a new phase does not appear in it. If the nuclei of a new, more stable phase are introduced into it,

a transition to this phase occurs. This is how supercooled liquids behave. Glassy bodies, being metastable, remain infinitely in this state.

The distinction is made between thermal, mechanical stability, and stability in respect of diffusion.

Thermal stability is the stability of a system in respect of thermal perturbations, and thermal equilibrium conforms to the equality of temperatures in all regions of a system. *Mechanical stability* is stability in respect of mechanical perturbations, and mechanical equilibrium conforms to the equality of pressures in all regions of a system.

For binary systems, the main type of stability is *stability in respect of diffusion*, i.e., in respect of the appearance of heterogeneities in composition. A mathematical criterion of this type of stability is the following inequalities:

$$\frac{d\mu_1}{dx_1} > 0; \quad \frac{d\mu_1}{dx_2} < 0; \quad \frac{d^2G}{dx_2^2} > 0 \tag{13.60}$$

In a stable binary system, the diffusion of a component may occur if its chemical potential $\mu_1 < \mu_1^0$, and it ends when $\mu_1 = \mu_1^0$. Hence, as the mole fraction of a given component increases in a solution, its chemical potential may increase only to the value of μ_1^0, i. e., the derivative $\frac{d\mu_1}{dx_1}$ is substantially positive, and the derivative $\frac{d\mu_1}{dx_2}$ is negative.

The inequality $\frac{d^2G}{dx^2} > 0$ has a simple geometrical meaning. If, for p, T = const, ΔG^m is plotted as a function of x_2, the second derivative in respect of composition may be positive if the curve of dependence $\Delta G^m = f(x_2)$ is concave down (curve *1* in Fig. 13.12*a*). In this case, $\Delta G^m < 0$. If $\Delta G^m > 0$, and the curve is concave up, the system is unstable in all compositions (curve *2* in Fig. 13.12*a*). If a curve has region *MN* which is concave up (curve *3* in Fig. 13.12*a*), the system is unstable in this composition region and separates into two phases whose composition conforms to points *A* and *B*.

If such curves are plotted for different temperatures, the locus of points *A* and *B* is curve *1* in Fig. 13.12*b*, known as a *binodal*. This is a curve of mutual mixing, which has been dealt with at length on page 352. The locus of points *M* and *N* is curve *2* in Fig. 13.12*b*, known as a *spinodal*. A binodal separates the region of stable states from the region of metastable states (*MN* region). A spinodal separates the region of metastable states from that of unstable states. A spinodal is the boundary of absolute instability of a system, and metastable states may often be regarded as

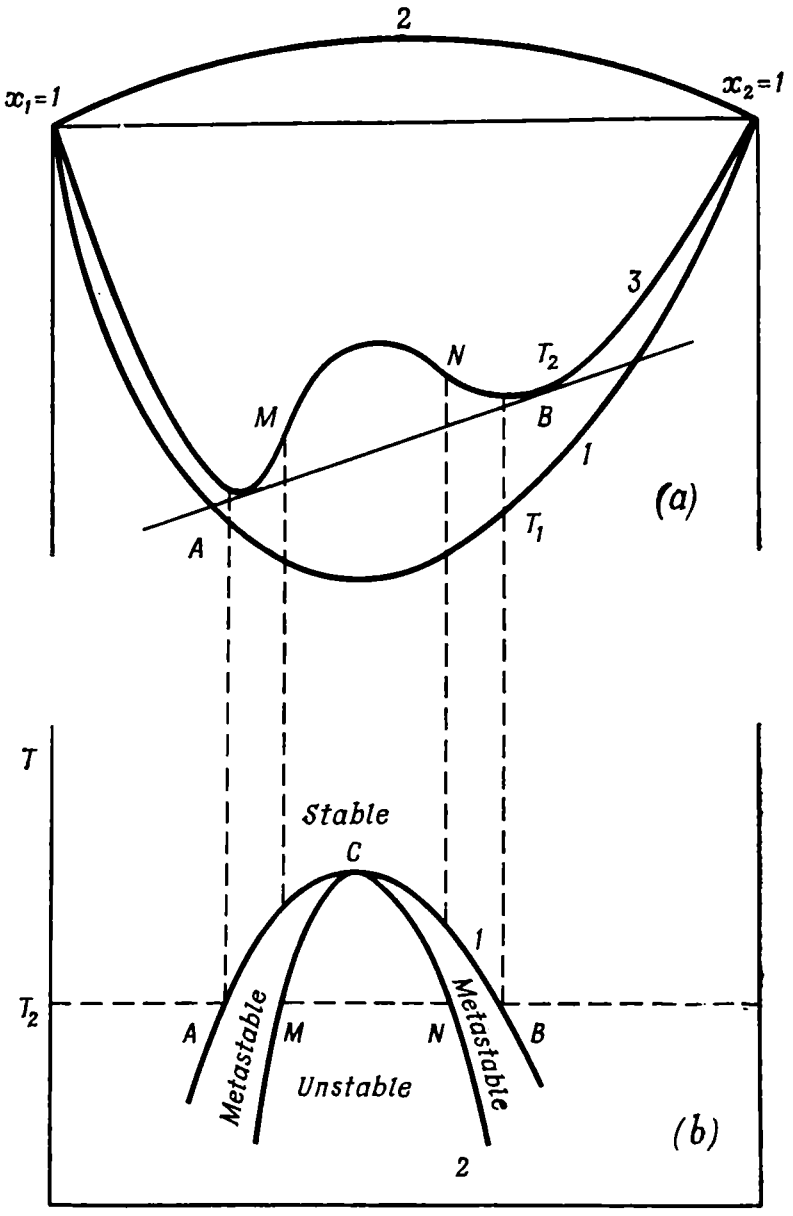

Fig. 13.12. Dependence of average free energy of mixing on composition (*a*) and phase equilibrium (*b*):
ACB — binodal; MCN — spinodal

stable. Prigogine and Defay wrote that they regarded stable phases proper and metastable phases as stable, since these phases possess some properties in common which distinguish them from unstable phases.

These principles are important in two respects. First of all, it follows from them that a thermodynamically stable system and a system in an equilibrium state are not the same thing. In a thermodynamically stable system, there are always changes in the

chemical potentials of components and free energy that conform to inequalities (13.60). For unlimitedly dissolving polymers, this is represented in Fig. 13.12. In an equilibrium state, $\Delta\mu_1 = \Delta\mu_2 = = \Delta G^m$.

Secondly, polymers and polymeric systems are often in metastable states, i.e., the states with a lower value of G conform to their equilibrium. However, as S. Ya. Frenkel correctly notes, such states of relative equilibrium may be regarded as equilibrium states if the parameters of a system in these states remain invariable for a sufficiently long time in comparison with the duration of an experiment. This makes it possible to apply thermodynamic relationships to metastable systems.

13.10. ENTHALPY OR HEAT OF MIXING

Enthalpy, or heat of mixing is the difference between the enthalpy of a solution and the sum of enthalpies of components:

$$\Delta H = H_{sol} - \sum H_i^0 n_i \qquad (13.61)$$

It is equal to the *integral heat of solution*, i.e., the heat of solution of a given amount of one component in a certain volume of another one at constant pressures and temperature ($\Delta H = Q_p$). The integral heat of solution is related to unit mass of a dissolved substance or to unit mass of a solution (to mole or gram), and is expressed in calories or joules.

If heat is generated, dissolution is said to be *exothermic*, and if heat is absorbed, it is *endothermic*. A dissolution process is said to be *athermal* when the heat effect is naught.

If heat is generated, enthalpy decreases ($\Delta H < 0$), and if heat is absorbed, enthalpy increases ($\Delta H > 0$). If $Q_p = 0$, then $\Delta H = 0$.

The *integral heat of dilution* is the heat generated or absorbed on dilution of a solution of definite concentration with a large amount of a solvent.

The *differential heat of solution* or *dilution* is the heat generated or absorbed when an infinitely small number of moles of component i is added to a solution of definite concentration, referred to 1 mole of that component:

$$\frac{q_i}{\delta n_i}$$

The differential heat of solution is equal to the change in partial enthalpy:

$$\frac{q_1}{\delta n_1} = \Delta H_1; \quad \frac{q_2}{\delta n_2} = \Delta H_2 \qquad (13.62)$$

If heat is generated, $\Delta H_i < 0$; if it is absorbed, $\Delta H_i > 0$; if $q_i = 0$, then $\Delta H_i = 0$.

The *integral heat of solution* of a polymer can be measured calorimetrically. This is done by mixing a weighed portion of a polymer with a definite amount of the low-molecular component in a calorimetric vessel. On coming in contact with the solvent the polymer swells and then dissolves. The entire procedure takes from 20 to 60 min, even if very small samples of a polymer are used.

TABLE 13.2. *Integral Heats of Solution and Swelling of Some Polymers at* 25 °C

Polymer	Molecular mass of polymer	Solvent	ΔH, cal/g
Polyisobutylene	30 000	*n*-Pentane	−0.86
		n-Hexane	−0.61
		n-Heptane	−0.43
		n-Octane	−0.29
		n-Tetradecane	0
Natural rubber		Benzene	1.36
		Gasoline	0.1
		Chloroform	−3.0
Poly(vinyl acetate)	93 000	Ethyl acetate	0
	93 000	Acetone	−0.11
Poly(vinyl alcohol)	17 000	Ethyl alcohol	2.3
	17 000	Water	−2.03
Polystyrene	142 000	Ethylbenzene	−3.8
	142 000	Benzene	−4.0
	20 000	Benzene	−3.69
	142 000	Toluene	−4.32
	20 000	Toluene	−3.99
	142 000	Xylene	−3.52
	20 000	Xylene	−3.20
	142 000	Methyl ethyl ketone	−3.96
	20 000	Methyl ethyl ketone	−3.65
	142 000	Acetone	−2.35
	20 000	Acetone	−2.51
	142 000	Ethyl acetate	−3.02
	20 000	Ethyl acetate	−2.62
Poly(methyl methacrylate)	3.06×10^6	Methyl isobutyrate	0
	3.06×10^6	Dichloroethane	−12
Cellulose	—	Water	−10.0
	—	Quaternary ammonium bases	−35.0
Cellulose nitrate	—	Acetone	from −18.0 to −19.2

The main difficulty of this method is that a very small amount of heat is generated or absorbed per unit time. Such measurements require precise instruments and great skill on the part of the operator. The use of large polymer samples is impracticable, because this considerably increases the viscosity of the resulting solutions, making it difficult to stir them, and, moreover, the time of the thermal reaction becomes prohibitively great. For this reason, in most studies integral heats of formation are determined for solutions containing not more than 0.1 weight fraction of a polymer.

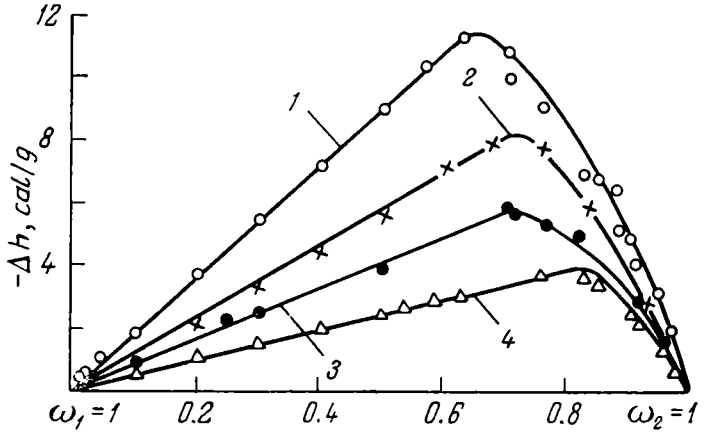

Fig. 13.13. Plots of Δh vs. ω_2 for polymer solutions:
1—cellulose nitrate-acetone; *2*—poly (methyl methacrylate)-dichloroethane; *3*—cellulose triacetate-chloroform; *4*—polystyrene-ethylbenzene

The integral heats of solution and swelling of several polymers are listed in Table 13.2, from which it follows that the solution of polymers may be athermal, exothermic or endothermic.

However, integral solution heats of polymer solutions can also be obtained over the whole range of concentrations.

Figure 13 13 shows Δh vs. ω_2 curves for a number of polymer-solvent systems over the whole range of compositions. It can be seen that these curves are similar to those of the integral heats of mixing of two low-molecular liquids, with the only difference that here the maximum is greatly shifted towards high weight fractions of the high-molecular components.

To obtain Δh vs. ω_2 dependencies the integral heats of solution in the dilute solution region are determined in the usual way (by breaking an ampoule containing a weighed portion of the polymer in the solvent) and the heats of solution in the concentrated solution region are calculated in accordance with the Hess law. For this purpose an accurately weighed portion of polymer (g_2, g) is placed in an atmosphere of the vapours of a low-molecular liquid until it absorbs a definite amount of the vapour (g_1, g). This results in a solution I containing the weight fraction of polymer

$\omega_2 = g_2/(g_1 + g_2)$. Its formation involves the heat effect Q_x. Solutions may be prepared with weight fractions of a polymer ranging from 1 to approx. 0.5.

To ensure uniform distribution of the components the solutions are held in sealed ampoules for 4 or 5 days, after which an ampoule containing the concentrated solution I is broken in a calorimeter containing a definite amount of the same solvent (m, g). This results in solution II and is accompanied by the generation or absorption of the *integral heat of dilution* q. Obviously, solution II can be obtained by dissolving the same amount of polymer g_2 in $m + g_1$ grams of the solvent directly in the calorimeter. These processes can be represented by the following thermochemical equations:

$$g_2,\ \text{g} + g_1,\ \text{g} = \text{solution I} + Q_x,\ \text{cal/g}$$

$$\text{solution I} + m,\ \text{g} = \text{solution II} + q,\ \text{cal/g}$$

$$g_2,\ \text{g} + (m + g_1),\ \text{g} = \text{solution II} + Q,\ \text{cal/g}$$

According to the Hess law,

$$Q_x + q = Q$$

whence

$$Q_x = Q - q \qquad (13.63)$$

Therefore to calculate the integral heat of solution generated during the formation of a concentrated solution, it is necessary to determine the integral heat of solution of the same polymer in a large amount of solvent and subtract the integral heat of dilution.

The more dilute the solution I (the smaller the weight fraction of polymer in it), the smaller will be the value of q, and at $\omega_2 \approx 0.6$ it becomes zero, and hence, $Q_x = Q$ [Eq. (13.63)].

To plot ΔH versus ω_2 graph the integral heats of solution referred to 1 g of solution are marked off along the ordinate. To obtain these values, one multiplies Q_x by the mass of a polymer placed in the ampoule and divides by the mass of a solution, i.e., one multiplies Q_x by the weight fraction of a polymer in solution I:

$$\Delta H \frac{\text{cal}}{\text{grams of solution}} = Q_x \frac{g_2}{g_1 + g_2} = Q_x \omega_2 \qquad (13.64)$$

13.11. DIFFERENTIAL HEATS OF SOLUTION AND DILUTION

Differential heats of solution can be determined experimentally (in calorimeters) or calculated.

Differential heats of solution and dilution of polymer solutions may be calculated by the intercept method described on p. 375 or by determining the differential heats of adsorption. In the former

case experimental data must be available on the integral heats of solution over the whole range of concentrations and the calculation is made from the ΔH versus ω_2 curve. The second method is as follows.

Suppose that before the calorimetric experiment the polymer absorbed g_1 grammes of vapour of the low-molecular component. We add a small quantity of vapour to the resulting solution to make g_1', g. This involves generation of an amount of heat equal to

$$\int_{g_1}^{g_1'} Q_a dg$$

where Q_a is the differential specific heat of dilution in cal/g.

Now we dilute the resulting concentrated polymer solution with a large amount of the same solvent (m_2) in a calorimeter and determine the integral heat of dilution q.

A similar solution can be prepared by dissolving the polymer directly in $(m + g_1')$ g of solvent. According to the Hess law the heat generated (Q) is

$$Q = \int_{g_1}^{g_1'} Q_a dg + q \quad (13.65)$$

whence

$$\int_{g_1}^{g_1'} Q_a dg = Q - q \quad (13.66)$$

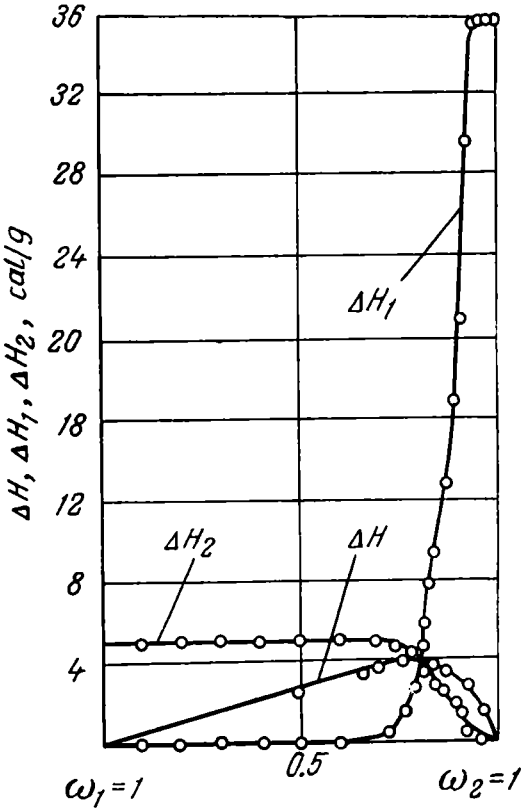

Fig. 13.14. Dependence of $-\Delta H$, $-\Delta H_1$, and $-\Delta H_2$ on composition for the system polystyrene-benzene

Differentiating both sides of Eq. (13.66), we get

$$Q_a = -\frac{dq}{dg_1} \quad (13.67)$$

since $\frac{dQ}{dg_1} = 0$.

Therefore, the differential heat of dilution is equal to the slope tangent of the integral heat of dilution versus composition curve.

Figure 13.14 shows typical ΔH_1 versus composition and ΔH_2 versus composition curves for a polymer solution. It follows from

the figure that at low polymer concentrations ΔH_1 is very small, but increases greatly with increasing concentration.

In a number of cases heats of solution are calculated from the Gibbs-Helmholtz equation which acquires the following form after integration under the assumption that the heat of solution is independent of temperature:

$$\Delta H_i = \frac{T_1 \Delta\mu_{iT_2} - T_2 \Delta\mu_{iT_1}}{T_1 - T_2} \tag{13.68}$$

where $\Delta\mu_{iT_2}$ and $\Delta\mu_{iT_1}$ are the differences of chemical potentials determined by one of the above-described methods at two temperatures.

Many investigators have pointed out that such calculations are inaccurate, the more so that the heat of solution of some polymers varies greatly with temperature.

13.12. ENTROPY OF MIXING

Entropy of mixing is the difference between the entropy of a solution and that of its components prior to mixing:

$$\Delta S_{\text{mix}} = S_{\text{sol}} - \sum S_{\text{comp}} \tag{13.69}$$

Partial entropy of mixing is the difference between the partial molar entropy of a component in solution and the molar entropy of the pure component:

$$\Delta S_{i\ \text{mix}} = S_i - S_i^0 \tag{13.70}$$

Entropy is a function connected with the number of modes of the arrangement of molecules, which may be due to their rearrangements or to a change in the order brought about by some fields, including intermolecular interaction. The entropy of mixing that concerns only the rearrangements of molecules is known as the *combinatorial entropy of mixing* ΔS_{comb}. It is always positive, since the number of modes of molecular arrangement is greater in a solution than in individual components due to the addition of rearrangements of different molecules ($\Delta S_{\text{comb}} > 0$), and this favours mixing.

Gibbs showed that when two ideal gases are mixed, the entropy per mole of the mixture increases by

$$\Delta S_{\text{mix}} = -R(N_1 \ln N_1 + N_2 \ln N_2) \tag{13.71}$$

The quantity ΔS_{mix} calculated from Eq. (13.71) is called the *ideal entropy of mixing* (the method of calculating it is described in Chap. 15).

Partial ideal entropies of mixing can be obtained by differentiating Eq. (13.71):

$$\Delta S_1 = \frac{\partial \Delta S}{\partial n_1} = -R \ln N_1$$
$$\Delta S_2 = \frac{\partial \Delta S}{\partial n_2} = -R \ln N_2 \qquad (13.72)$$

In real solutions, however, random arrangement of molecules is impossible. There are always some pre-eminent arrangements as a result of intermolecular interaction, i.e., either the solution is more ordered than the components or, conversely, disorder in molecular arrangement is observed upon dissolution. In the first case, entropy decreases upon dissolution, and in the second, it increases.

The contribution of entropy due to the energy of interaction is known as the *noncombinatorial entropy of mixing*. It follows that $\Delta S_{\text{noncomb}}$ may be positive and negative. The total entropy of mixing is the sum of both contributions,

$$\Delta S^{\text{m}} = \Delta S_{\text{comb}} + \Delta S_{\text{noncomb}} \qquad (13.73)$$

and depends on their relation. Therefore, it may likewise be positive and negative. In the latter case, it does not favour mixing.

In most cases Eqs. (13.71) and (13.72) are not valid for dissolution of polymers, nor for mixing of low-molecular liquids, and the entropy of mixing is calculated as the difference between the experimental values of ΔH and ΔG:

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (13.74)$$

$$\Delta S_i = \frac{\Delta H_i - \Delta \mu_i}{T} \qquad (13.75)$$

The values of ΔS calculated in this way for polymer solutions are always lower than their values for mixtures of low-molecular liquids. This is due to the low mobility of units bound chemically into long chains, compared to the mobility of monomer molecules. The restricted freedom of movement of the units of a polymer chain results in the number of ways of arranging different molecules in the polymer solution, or the thermodynamic probability of the system, being smaller than in solutions of its low-molecular analogue.

13.13. CHANGE IN VOLUME ON DISSOLUTION OF POLYMERS

The change in volume accompanying dissolution or mixing of liquids depends on the composition of the solution. Four cases are possible, analogous to the change in enthalpies:

(1) $\Delta V = 0$ over the whole range of compositions;

(2) $\Delta V > 0$ over the whole range of compositions (expansion);
(3) $\Delta V < 0$ over the whole range of compositions (contraction);
(4) contraction in one range of compositions ($\Delta V < 0$) and expansion in another ($\Delta V > 0$).

The change in volume is associated with a change in distances between molecules and may be due to the following causes: (1) difference in energies of attraction of the component molecules in the isolated state and in molecular mixture: the higher the attraction in the mixture, the smaller the volume; (2) difference in

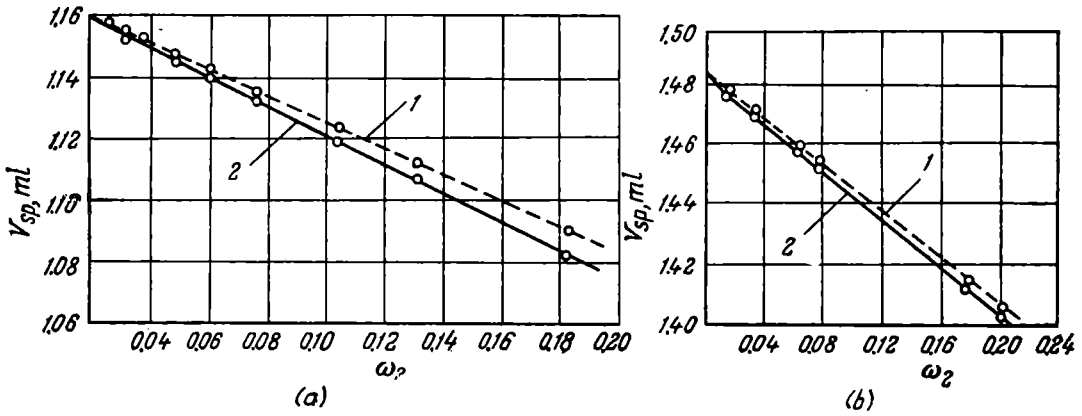

Fig. 13.15. Change in volume of polystyrene-ethylbenzene (*a*) and polyisobutylene-isooctane (*b*) solutions depending on their composition:
1—additive change in volume; *2*—actual change in volume

molecular packing prior to mixing and in solution, this being related to the geometry of the molecules; (3) difference in molecular packing due to different sizes of the molecules.

The last two factors are called *geometrical factors*. The first to draw attention to their importance was Mendeleev. The total change in volume upon mixing is made up of the changes caused by attraction or repulsion between molecules (ΔV_{inter}) and changes resulting from geometrical factors (ΔV_{geom}).

$$\Delta V^{\text{m}} = \Delta V_{\text{inter}} + \Delta V_{\text{geom}} \qquad (13.76)$$

These terms may differ in sign as well as in magnitude.

The role of the geometrical factor for a number of liquid-liquid systems has been demonstrated in recent years, but it is especially important for polymer-solvent systems.

As was indicated above, owing to the difference in molecular size, a polymer possesses a smaller free volume than a low-molecular liquid (p. 170). On dissolving, the polymer passes into a medium with a greater free volume and so expands, as it were, whereas the solvent passes into a medium with a smaller free volume and therefore contracts. The net effect should depend on

the relation of these processes, so that either contraction or expansion may be expected upon dissolution of polymers.

Contraction during solution of polymers was first observed experimentally in 1955. The relevant data are given in Fig. 13.15 for solutions of polystyrene and polyisobutylene in their own hydrogenated monomers, ethyl benzene and isooctane, respectively. In these systems interaction between like and unlike molecules is the same, and hence, the change in volume depends on geometrical factors. It is evident from the figure that the loosely packed polymer, viz., polystyrene, dissolves with greater contraction than closely packed polyisobutylene.

Contraction is observed when polyisobutylene dissolves in isooctane, *n*-hexane, *n*-neptane, and *n*-decane, cyclohexane, and methylcyclohexane. Dissolving of polyisobutylene in benzene, and toluene and chlorobenzene involves expansion, like dissolution of natural rubber in benzene.

13.14. INTERNAL ENERGY OF MIXING

Knowing the volumes of mixing ΔV^{m}, one can calculate all the thermodynamic functions at constant volume, which is very important. For example, one can calculate the internal energy of mixing $(\Delta U^{m})_V$ or the Helmholtz free energy of mixing $(\Delta F^{m})_V$. Let us carry out such a calculation for $(\Delta U)_V$.

Enthalpy of mixing $(\Delta H)_p$ is related to the internal energy of mixing by the equation

$$(\Delta H)_p = (\Delta U)_p + p_i (\Delta V)_p \tag{13.77}$$

which can be transformed into an equation containing $(\Delta U)_V$ as one of its terms. To do so we make use of the well-known thermodynamic relation

$$p = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial p}{\partial T}\right)_V \tag{13.78}$$

Substituting the value of p from Eq. (13.78) into Eq. (13.77), we obtain

$$(\Delta H)_p = (\Delta U)_p - \left(\frac{\partial U}{\partial V}\right)_p (\Delta V)_p + T\left(\frac{\partial p}{\partial T}\right)_V (\Delta V)_p \tag{13.79}$$

To a first approximation,

$$(\Delta U)_p = (\Delta U)_V + \left(\frac{\partial U}{\partial V}\right)_p (\Delta V)_p \tag{13.80}$$

Hence,

$$(\Delta H)_p = (\Delta U)_V + T\left(\frac{\partial p}{\partial T}\right)_V (\Delta V)_p \tag{13.81}$$

Since volume changes in the condensed state are small, the second terms in Eqs (13.77) and (13.81) were usually neglected, and it was thought that

$$(\Delta H)_p = (\Delta U)_p = (\Delta U)_V \tag{13.82}$$

This is a crude error, for the values of p_i and $(\partial p_i/\partial T)_V$ are very high and therefore the contribution of the second term to the value of $(\Delta H)_p$ is also large. The quantity p_i is the internal pressure of the liquid, and $(\partial p_i/\partial T)_V$ is the thermal coefficient of pressure, equal to the ratio of the volume expansion coefficient of the liquid α_p to the coefficient of isothermal compressibility β_T:

$$\gamma \equiv \left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha_p}{\beta_T} \tag{13.83}$$

For such low-molecular liquids as benzene or ketone and also for polymer solutions it is approximately 10 atm/deg, which, multiplied by 300 (room temperature), gives a value of 3000 atm. Therefore, even if the change in volume involved in mixing liquids or dissolving polymers is about 1 per cent of the volume of the system, both $(\Delta H)_p$ and $(\Delta U)_V$ may differ considerably from each other. For example, the heat of mixing of benzene with cyclohexane, measured at constant pressure, $(\Delta H)_p = 186$ cal, and at constant volume, $(\Delta U)_V = 131$ cal.

Note the difference between Eqs. (13.77) and (13.81). The former is used to calculate the value of $(\Delta U)_p$, and the latter, of $(\Delta U)_V$, which are not equal in the general case. Equality of these two quantities is essentially tantamount to the equation

$$p_i = \frac{\alpha_p}{\beta_T} \cdot T \tag{13.84}$$

which, as Ioffe and Semenov have shown, does not always give correct results.

Thus, the values of p_i calculated by Eq. (13.84) for ether and ethyl chloride are in agreement with the data obtained by other measurements within a margin of 10 to 15 per cent. However, in the case of mercury and other metals, as well as for water, the values of p_i, calculated from Eq. (13.84), are almost twice as small as the values obtained by other methods. Hence, in such systems the values of $(\Delta U)_p$ and $(\Delta U)_V$ differ.

Attempts have been made in recent years to calculate $(\Delta U)_V$ for mixtures of low-molecular liquids, as well as for polymer solutions. To do so it is necessary to know p_i and γ of both the initial components and their mixtures.

In the case of dilute polyisobutylene solutions Bianchi and coworkers considered p_i equal to the internal pressure of the

solvent and calculated $(\Delta U)_V$ on the assumption that the right-hand sides of Eqs. (13.77) and (13.81) are equal, which, as has already been shown, is in general wrong. In the case of the systems they investigated the values of $(\Delta U)_p$ and $(\Delta U)_V$ were, however, actually equal.

Very interesting studies in this line were carried out by Malcolm and coworkers, who studied solutions of alkylated poly(hydroxyethylene glycol)s and poly(hydroxypropylene glycol)s in chloroform and carbon tetrachloride. They determined experimentally the thermal coefficients of pressure for the initial substances and solutions, and found them to be between 12 and 14 atm/deg; they showed that the γ of the mixture is the additive sum of the components γ, i.e.,

$$\gamma^m = \varphi_1\gamma_1 + \varphi_2\gamma_2 \tag{13.85}$$

where φ_1 and φ_2 are the volume fractions of a solvent and a polymer.

Very high negative values of $(\Delta H)_p$ and $(\Delta U)_V$ are observed for solutions of methylated polyethers in organic liquids. Depending on the nature of a solvent the entropy of mixing may be either positive ($T\Delta S > 0$) or negative ($T\Delta S < 0$).

Solutions of oligomeric polyhydroxyalkylenediols in water display very high negative values of $(\Delta H)_p$, $(\Delta U)_V$, and $(\Delta S)_V$ with a compensation effect, i.e., the terms $(\Delta H)_p$ and $(T\Delta S)_V$ offset each other, so that the value of $\Delta G = \Delta H - T\Delta S$ is comparatively small.

Internal energy U is an important thermodynamic parameter which includes the kinetic and potential energies of a system. The latter is the totality of energies of interaction of all the elements of a system: molecules with one another, atoms inside a molecule, electrons with the nucleus and with one another, and so forth. On dissolution, which occurs at constant volume and temperature, the energies of all interactions, except intermolecular ones, do not undergo substantial changes. The latter changes, because solvent-solvent and polymer-polymer contacts are replaced by polymer-solvent contacts.

Suppose the bond energy of one mole of solvent molecules is E_{11}, the bond energy of one mole of polymer chain units is E_{22}, and the bond energy of one mole of chain units and the solvent is E_{12}. When one mole of polymer units is mixed with one mole of the solvent, in order to rupture contacts, energy $(E_{22} + E_{11})$ is spent and energy $2E_{12}$ is liberated as new contacts are formed. Then, the total change in internal energy $(\Delta U^M)_V$ should be proportional to the algebraic sum of these quantities:

$$-(\Delta U^M)_V = K[-E_{11} - E_{22} + 2E_{12}] \tag{13.86}$$

If in terms of absolute values,

$$|E_{11}+E_{22}|=|2E_{12}|, \text{ then } (\Delta U^{M})_V=0 \qquad (13.87a)$$

$$|2E_{12}|>|E_{11}+E_{22}|, \text{ then } (\Delta U^{M})_V<0 \qquad (13.87b)$$

$$|E_{11}+E_{22}|>2E_{12}, \text{ then } (\Delta U^{M})_V>0 \qquad (13.87c)$$

Consequently, when the cohesion energies of a polymer and of a solvent are equal (polymer-hydrated monomer system), the internal energy may not change, but since this is accompanied by compression, then $\Delta H<0$, and heat is generated on dissolution. This is observed, for example, when polyisobutylene and polystyrene are dissolved in their hydrated monomers. It follows that exothermal dissolution is far from always the outcome of the preferential energy polymer-solvent interaction. It may be the result either of a change in volume or of the preferential polymer-polymer contacts if polymer crystallization occurs on dissolution.

13.15. VARIATION OF THERMODYNAMIC AFFINITY OF A POLYMER TO A SOLVENT WITH TEMPERATURE. CRITERIA OF UCST AND LCST

The thermodynamic affinity of a solvent to a polymer changes with temperature, and this predetermines the type of critical solution temperature. That is clearly seen in Fig. 13.16. If the positive values of the second Virial coefficient A_2 and the negative values of ΔG^{m} decrease as temperature drops, it may be predicted that the system will separate into phases on cooling, i.e., UCST is observed. If the positive values of A_2 and the negative values of ΔG^{m} decrease as temperature rises, the system will separate on heating, i.e., it possesses LCST. If a growth in A_2 and ΔG^{m} is observed in the lower temperature range and if these parameters decrease with temperature in the higher temperature range, the system will have a phase diagram in the form of a closed contour. Finally, if A_2 and ΔG^{m} change with temperature in a way shown in Fig. 13.16*d*, the system has a phase diagram with LCST greater than UCST.

It follows from Fig. 13.17 that the second Virial coefficient A_2 of a solution of polystyrene in cyclohexane increases with a rise in temperature; consequently, separation may be expected on cooling. This system really possesses UCST in the temperature range close to the considered one. The value of A_2 of a solution of polyisobutylene in pentane and many other solutions (Fig. 13.17) decreases as temperature rises; hence, these systems possess LCST. The values of A_2 of the solution of polyisobutylene in dibutyl ether change according to the curve with the maximum; it follows that

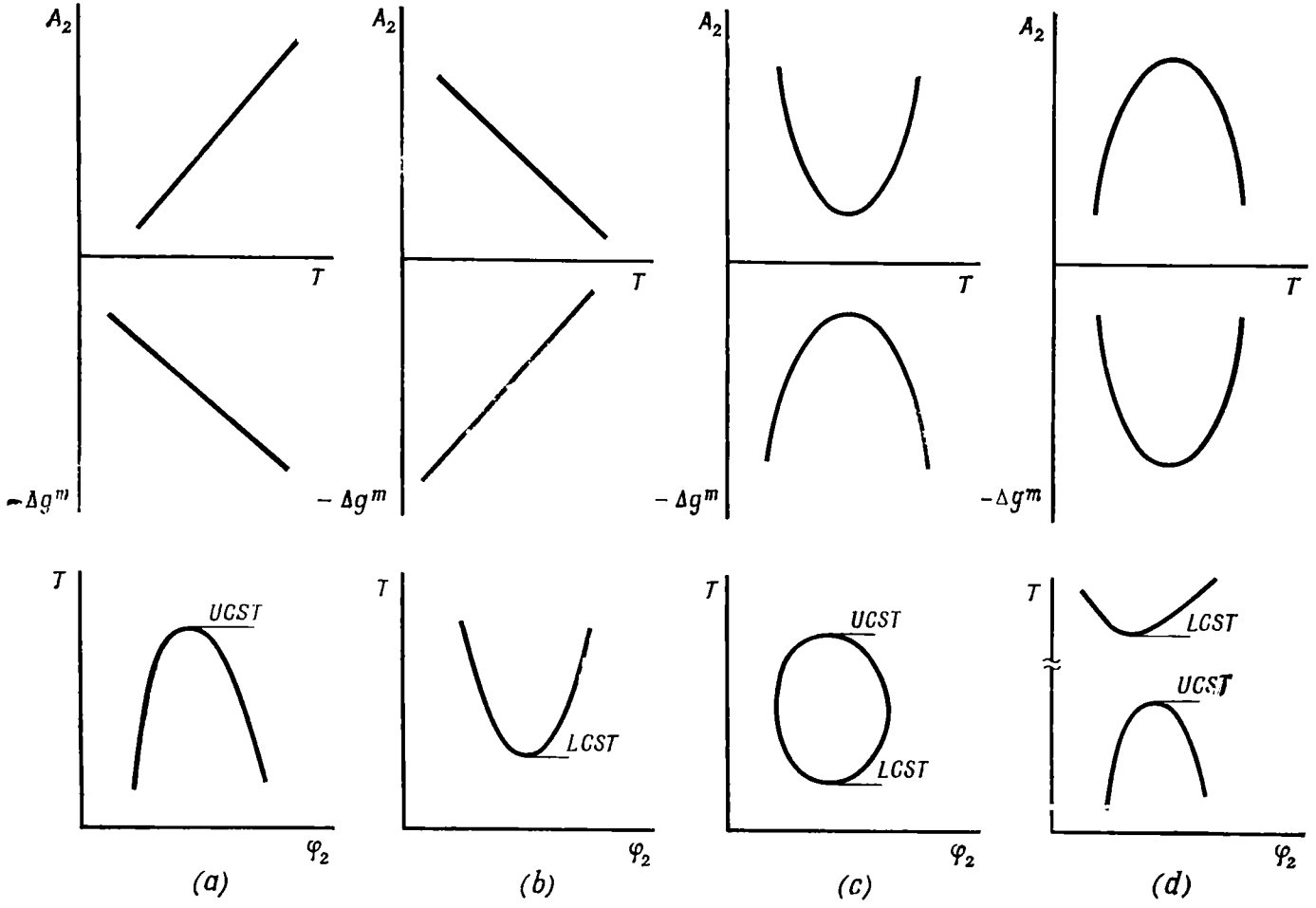

Fig. 13.16. Change in the second Virial coefficient A_2 and ΔG^m with the temperature and the type of critical solution temperature

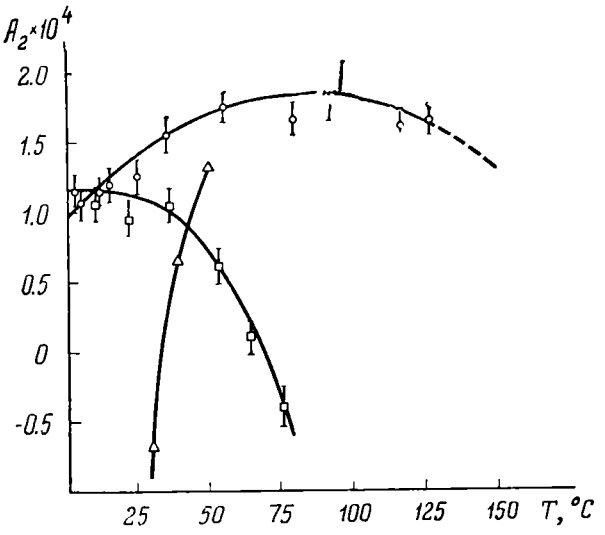

Fig. 13.17. Temperature dependence of second Virial coefficient:
△—polystyrene-cyclohexane, ○—polyisobutylene-dibutyl ether, □—polyisobutylene-*n*-pentane

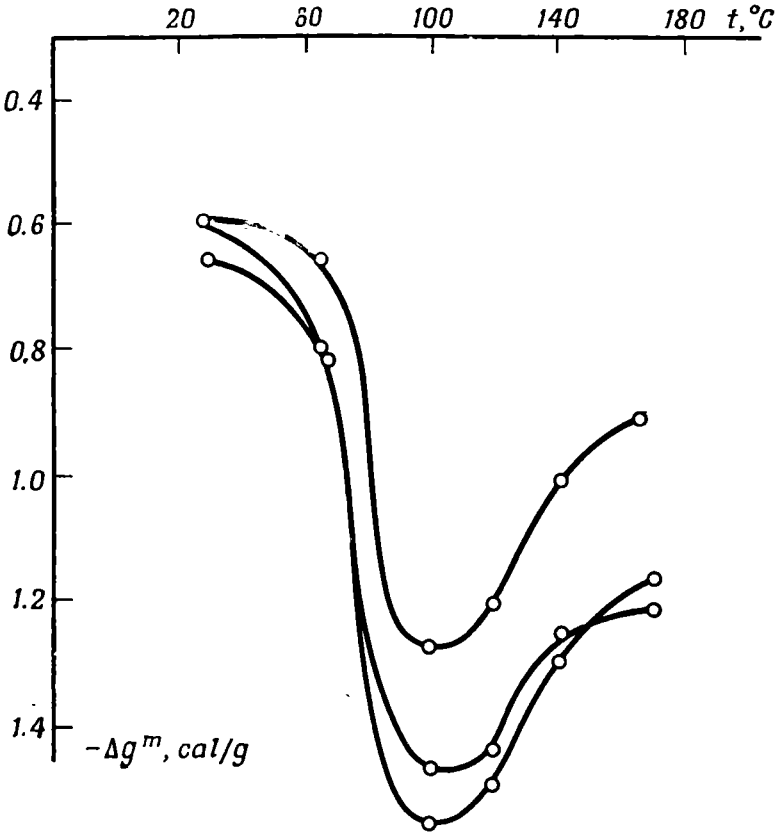

Fig. 13.18. Change in excess enthalpies and entropies of mixing with temperature and the type of critical solution temperature (scheme)

this system possesses UCST and LCST. In a wide temperature range, the free energy of mixing of the polystyrene-cyclohexane system likewise changes extremely with a rise in temperature (Fig. 13.18); as a result, the system separates on cooling and on heating.

Deterioration of mutual solubility of components implies a growth in positive deviations from ideality (p. 380), i.e., a growth in the positive values of excess free energy G^E. If affinity deteriorates on heating, then $\frac{\partial G^E}{\partial T} > 0$, and if it does so on cooling, then $\frac{\partial G^E}{\partial T} < 0$. Therefore, regardless of the type of CST, a system is characterized by positive deviations from ideality on separation; in this case, $G^E \cong \frac{1}{2} RT$.

All this shows that the phase separation of the polymer-solvent system does not occur spontaneously, but is prepared long before its onset, being the result of structural changes in homogeneous solutions.

It is known that

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{and} \quad \left(\frac{\partial \left(\frac{G}{T}\right)}{\partial T}\right)_p = -\frac{H}{T^2} \qquad (13.88)$$

The same relations can be written for excess thermodynamic functions:

$$\left(\frac{\partial G^E}{\partial T}\right)_p = -S^E \quad \text{and} \quad \left(\frac{\partial \left(\frac{G^E}{T}\right)}{\partial T}\right)_p = -\frac{H^E}{T^2} \qquad (13.89)$$

where S^E and H^E are the excess entropy and enthalpy of mixing.

It follows from the above that:

(a) an upper critical solution temperature ($\partial G^E/\partial T < 0$) is possible under the condition that $S^E > 0$ and $H^E > 0$, i.e., with endothermic mixing and an increase of entropy;

(b) a lower critical solution temperature can be observed if $S^E < 0$ and $H^E < 0$, i.e., with exothermic mixing and a decrease of entropy.

Prigogine and Defay have suggested a more rigorous criterion of the type of the critical solution temperature, namely

$$\text{UCST} \quad \frac{d^2h}{dx_2^2} < 0 \quad \text{and} \quad \frac{d^2s}{dx_2^2} < 0$$

$$\text{LCST} \quad \frac{d^2h}{dx_2^2} > 0 \quad \text{and} \quad \frac{d^2s}{dx_2^2} > 0$$

In these inequalities x_2 is the mole fraction of the second component, h and s are the average enthalpies and entropies of mixing (p. 375). These criteria mean that if there is a UCST in the system, the composition vs. average enthalpy and average entropy curves are concave to the abscissa, i.e., heat is absorbed and the excess entropy is positive; in the case of LCST the composition vs. average enthalpy and average entropy curves are convex to the abscissa, i.e., heat is generated and the excess entropy is negative.

Note that a negative excess of enthalpy of mixing and a positive excess of entropy of mixing favour dissolution, because under such conditions the term ΔG in the equation $\Delta G = \Delta H - T\Delta S$ becomes more negative. Hence, the more essential conditions are: $S^E < 0$ for lower critical temperature and $H^E > 0$ for upper critical temperature.

Thus, knowing the sign of the entropy and enthalpy of mixing for a polymer-solvent system, one can predict whether it will have an upper or lower critical solution temperature.

In some systems the necessary thermodynamic criteria are observed long before these temperatures are reached; in others, the sign of H^E and S^E may change when the temperature is changed.

For example, polyisobutylene dissolves in lower alkanes exothermally even at room temperature (Table 13.2), and $S^E > 0$. With increasing temperature both H^E and S^E become more negative and S^E changes its sign.

Polystyrene dissolves in cyclohexane with absorption of heat ($H^E > 0$), which corresponds to an upper critical temperature in this system. In aromatics polystyrene dissolves exothermally, $H^E < 0$ and $S^E < 0$. Hence, one would expect phase separation to occur on heating which has recently been observed (see Fig. 12.4).

In the case of systems possessing both UCST and LCST the temperature coefficient $(\partial G^E/\partial T)_p$ should have different signs in different temperature regions. If the system is characterized by the phase diagram shown in Fig. 12.3*b*, i.e., UCST < LCST, the quality of solvent should improve at first with increasing temperature, and then grow worse. All this can be seen clearly in Fig. 13.17, which shows the temperature dependence of the second Virial coefficient—a parameter reflecting the quality of solvent.

Thus, in the case of the system polystyrene-cyclohexane A_2 increases with rising temperature in the temperature range close to UCST, which is generally observed for many polymer-solvent systems. At temperatures much below the LCST of the systems PI-*n*-pentane, A_2 declines with rising temperature. The same is observed in the system polystyrene-toluene. Delmas and Patterson

found an extremal dependence of A_2 for the system polyisobutylene-dibutyl ether.

A change in sign of $(\partial G^E/\partial T)_p$ with temperature means that the sign of H^E and S^E should change, which has also been observed for several systems.

The change in sign of the excess of enthalpy and entropy of mixing with temperature depends on the sign of the excess heat capacity:

$$\frac{\partial H^E}{\partial T} = c_p^E \quad \text{and} \quad \frac{\partial S^E}{\partial T} = \frac{c_p^E}{T}$$

If the heat capacity of the solution is equal to the sum of the heat capacities of the components, i.e., $c_p^E = 0$, the enthalpy and entropy of mixing are independent of temperature.

If the heat capacity of the solution is greater than the sum of the heat capacities of the components, then

$$\frac{\partial H^E}{\partial T} > 0 \quad \text{and} \quad \frac{\partial S^E}{\partial T} > 0$$

If the heat capacity of the solution is less than the sum of the heat capacities of the components, $c_p^E < 0$, $\frac{\partial H^E}{\partial T} < 0$, and $\frac{\partial S^E}{\partial T} < 0$.

13.16. THERMODYNAMICS OF DISSOLUTION OF POLYMERS AND THEIR STRUCTURE

The parameters ΔH, ΔS, ΔU and ΔV may have different signs, while the parameter ΔG must be negative on spontaneous dissolution. This is possible in three cases:

(1) $\Delta H_i < 0$ (heat is generated), $\Delta S_i > 0$ (entropy increases);

(2) $\Delta H_i < 0$, $\Delta S_i < 0$ (entropy decreases); in this case $|\Delta H_i| > |T\Delta S_i|$;

(3) $\Delta H_i > 0$ (heat is absorbed), $\Delta S_i > 0$ (entropy increases); here $|T\Delta S_i| > |\Delta H_i|$.

Hence, from the standpoint of thermodynamics, the solubility of polymers at constant temperature depends on the relationship of the enthalpy and entropy of mixing. Let us see how these parameters are affected by the elements of structure of a polymer which determine its solubility.

Chain Flexibility. Flexible-chain polymers have, as a rule, low polarity and dissolve in nonpolar or low-polar liquids. Thus, as Table 13.2 shows the enthalpies of mixing may have different signs, but they are always small. However, if there are flexible chains, it becomes possible for their units to exchange places with the molecules of a solvent; this leads to large positive values of the combinatorial entropy of mixing, which by its value may be hundreds of times higher than the ideal entropy of mixing

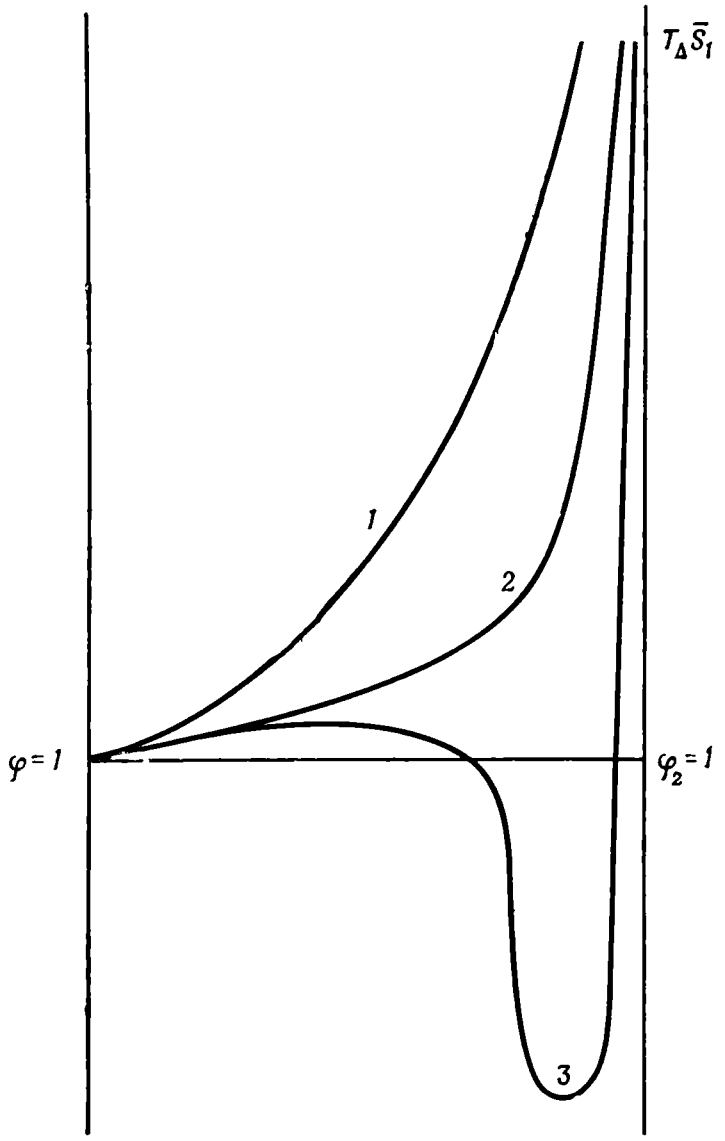

Fig. 13.19. Change in partial entropy with composition:
1—for solutions of flexible-chain polymers; *2*—of rigid-chain polymers; *3*—loosely packed polymers

(Table 13.3). It is the entropy factor that favours the dissolution of flexible-chain polymers, which unlimitedly mix together with liquids that are close to them by polarity.

The noncombinatorial entropy of mixing decreases (curve *2* in Fig. 13.19) as chain rigidity increases. Therefore, rigid-chain polymers may dissolve only when the energy of their interaction with a solvent is sufficiently large, i.e., when condition (2) is observed. However, if there is a very strong interaction between a polymer and a solvent, causing the orientation of molecules of the latter, the noncombinatorial entropy of mixing, which is negative in this

TABLE 13.3. *Partial Entropies of Mixing of Rubber and Toluene at* 25 °C

ω.	$N_2 \times 10$	$T\Delta S_1$, cal/mole	
		ideal	experimental
0.3	0.146	0.086	5
0.4	0.227	0.134	12
0.5	0.341	0.201	37
0.6	0.512	0.302	88
0.7	0.795	0.468	178
0.8	1.36	0.802	321
0.9	3.06	1.81	687
0.95	6.43	3.79	950

case, begins to play its role. This may lead to a negative value of the total entropy of mixing, especially in the region of high concentrations of a polymer in a solution. In this case, the concentration dependence of the entropy of mixing is expressed by curve *3* in Fig. 13.19, which in the dilute solution region passes over to the positive region. The negative values of the entropy of mixing are characteristic of the dissolution of many rigid-chain polar polymers (Table 13.4). In some cases, they are so large that $|T\Delta S| > |\Delta H|$ and then dissolution ceases. This is usually the cause of the limited swelling of rigid-chain polymers.

TABLE 13.4 *Variation of Some Thermodynamic Functions in Polymer-Water Systems (water content* 5.66%)

Polymer	Temperature, °C	ΔH_1, cal/mole	ΔZ_1, cal/mole	$T\Delta S_1$, cal/mole
Agar-agar	5	—3200	—1850	—1350
Casein	5	—2050	—900	—1150
Hair keratin	5	—2250	—1200	—1050
Wool keratin	20	—2800	—1400	—1400
Cellulose	50	—1000	—230	—770

The *dissolution of crystalline bodies* differs from the mixing of liquids in that the initial components are in different phase states, and a phase transition of one of them, i.e., melting, occurs on dissolution. Heat exactly equal to the heat of melting is expended always on the destruction of a crystalline lattice, and a dissolved substance passes over to a state of a supercooled liquid. Therefore, the partial heat of dilution of a crystalline body ΔH_2 is

usually represented in the form of a sum of two quantities, i.e., the heat of melting ΔH_2^{melt} and the partial heat of mixing of a supercooled liquid with a solvent ΔH_2^m:

$$\Delta H_2 = \Delta H_2^{melt} + \Delta H_2^m \tag{13.90}$$

In conformity with this, the quantity of the average enthalpy of dilution per mole of a solution is

$$\Delta h_{sol} = x_2 \Delta H_2^{melt} + \Delta H^m \tag{13.91}$$

The first term of Eqs. (13.90) and (13.91) is always positive, while the second term may have different signs. Depending on the relationship of ΔH_2^{melt} and ΔH^m, crystalline bodies, including crystalline polymers, may dissolve with the absorption or generation of heat.

A change in entropy on the dilution of crystalline polymers is also the sum of the entropy of melting and the entropy of mixing of a supercooled liquid. The first term is always positive, since the number of modes of molecular arrangement in a melt is considerably greater than in a crystalline lattice. This promotes an increase in the negative quantity ΔG and, consequently, the spontaneous dissolution of crystalline polymers, which occasionally occurs only on heating, when the term $T\Delta S$ becomes sufficiently large.

If the heats of dilution of a crystalline polymer and its amorphous modification are determined in the same liquid, the term ΔH^m will be the same, and then the heat of melting or crystallization may be determined by the difference between their partial heats of dilution. This was how the heats of crystallization of natural rubber, polyurethanes and other crystalline polymers were determined.

If we are interested in the heat of interaction of a crystalline polymer with different liquids, i.e., the quantity ΔH^m, it is necessary to subtract the heat of melting of a polymer from the experimentally determined partial heat of dilution $\Delta \bar{H}_2$.

An interesting phenomenon is observed during the dissolution of polymers which are capable of crystallization but for some reason have not crystallized. They begin to crystallize on contact with a thermodynamically poor solvent. This phenomenon is due to poor interaction with a solvent and the tendency of macromolecules to interact with one another. The presence of small molecules facilitates the mobility of macromolecules, which is necessary for the formation of an ordered structure of a polymer. In such cases, when a polymer interacts with a solvent, the heat of melting is

generated, and heat generation ($\Delta H < 0$) is calorimetrically detected, although the energy of polymer-solvent contacts is very small. As a result of ordering of a system during crystallization, the entropy of such a system decreases ($\Delta S < 0$) on interaction with a solvent.

Polymer crystallization in a solution may be observed also when the thermodynamic affinity of a solvent deteriorates with a change in temperature, say on cooling. Therefore, during crystal separation (p. 149) in a temperature range which precedes the separation of a system into two phases, polymer dissolution is accompanied with heat generation caused by crystal nucleation.

This phenomenon is similar to the formation of the so-called *hydrophobic bond*, i.e., a bond between the molecules of water and of hydrocarbons. These liquids are very poorly miscible, as a result of which the arrangement of water molecules becomes ordered near hydrocarbon molecules. Ultramicroscopic crystalline particles ("icebergs") are then formed, and this leads to heat generation. Such a phenomenon may occur in a polymer-water or polymer-organic solvent system if miscibility sharply deteriorates. Every component may form ordered aggregates from its own molecules, and this leads to heat generation.

Hence, exothermic mixing may be the result of not only the predominant formation of polymer-solvent contacts, but also the formation of polymer-polymer and solvent-solvent contacts.

The *glassy state*, being a thermodynamically nonequilibrium one, may exist infinitely long. In this case, macromolecule packing is more loose than equilibrium packing. For example, the volume of one gram of glassy polystyrene at 25 °C is 0.9413 cm^3 and that of equilibrium polystyrene under the same conditions is 0.9336 cm^3. It follows that macromolecules in real polystyrene are at distances greater than equilibrium distances. Since the energy of intermolecular interaction is inversely proportional to distance to the sixth power, an inconsiderable change in distances should lead to considerable changes in cohesion energy, which should be lower in a glassy polymer than in an equilibrium polymer; moreover, it should be less than the cohesion energy of a structurally similar low-molecular liquid at the same temperature. Hence, $E_{22} \ll E_{11}$; therefore, in conformity with Eq. (13.88), during the dissolution of a glassy polymer in its low-molecular analogue, it may be expected that ΔU^m will not be equal to zero, but $\Delta U^m < 0$. In this case, compression is observed, i.e., $\Delta V^m < 0$. Hence, $\Delta H^m < 0$.

Indeed, loosely packed glassy polymers, such as polystyrene, dissolve in their hydrogenated monomers and in most low-molecular liquids with heat generation (Table 13.2).

Jenkel proposed to represent, by analogy with Eq. (13.91), the heat of dissolution of a glassy polymer in the form of a sum of

two terms: the heat of glass transition ΔH_g and the partial heat of mixing:

$$\Delta h_2^g = x_2 \Delta H_g + \Delta H_2^m \qquad (13.92)$$

The *heat of glass transition* * is the difference between the heat of dilution of a polymer with nonequilibrium packing and that of an equilibrium glassy polymer; it must be equal to the heat of dilution of a polymer in a hydrogenated monomer, which is generated only due to the nonequilibrium packing of the polymer. To estimate the heat of mixing of a polymer with other liquids, the

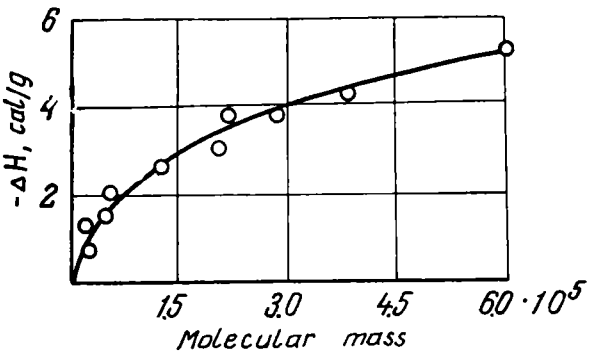

Fig. 13.20. Effect of the molecular mass of a polymer on the heat of mixing

value of the heat of its solution in a hydrogenated monomer (polystyrene in ethyl benzene) should be subtracted from the experimentally obtained values of Δh_2^g. In this case, $\Delta H^m > 0$ for several polystyrene-solvent systems, and this correlates with the presence of UCST.

A loosely packed polymer behaves like a microporous sorbent (p. 606); oriented adsorption layers are formed in the micropores of this sorbent at the initial stage of swelling, and this is accompanied with a decrease in entropy. The concentration dependence of $T\Delta S$ is expressed by curve *3* in Fig. 13.19. The entropy of mixing does not favour the dissolution of polymers which occurs due to the fact that $\Delta H < 0$ and $\Delta H > T\Delta S$.

The heat of dilution is a very sensitive parameter in respect of the density of polymer packing, and a change in this density may be detected by measuring the heats of dilution of polymers.

Molecular Mass of a Polymer. According to the congruence principle, the positive heat effect of mixing of hydrocarbons with one another increases as the difference of the dimensions of the components being mixed grows. Therefore, there should be enor-

* This term is not quite accurate, since glass transition is not a phase transition.

mous endothermal effects when polymer hydrocarbons dissolve in alkanes; however, they are not observed. Apparently, this principle is effective up to certain values of molecular masses, beginning with which the specific properties of a polymer engendered by chain flexibility are manifested. As the molecular mass of a polymer increases further, the heat of dilution becomes a less positive or even a more negative quantity. The latter is observed during the dissolution of polystyrenes and poly(methyl methacrylates) of different molecular mass (Fig. 13.20). However, this does not favour dissolution, since the combinatorial entropy of mixing decreases as the molecular mass of a polymer increases (Fig. 13.21). That occurs, because the chemical bonds between chain units confine the mobility of the latter, and the number of rearrangements between units and solvent molecules decreases. As the exothermal effect increases, the noncombinatorial entropy of mixing becomes negative, i.e., the quantity ΔS decreases. Therefore, as the molecular mass of a polymer increases, the free energy of mixing becomes less, i.e., solubility deteriorates.

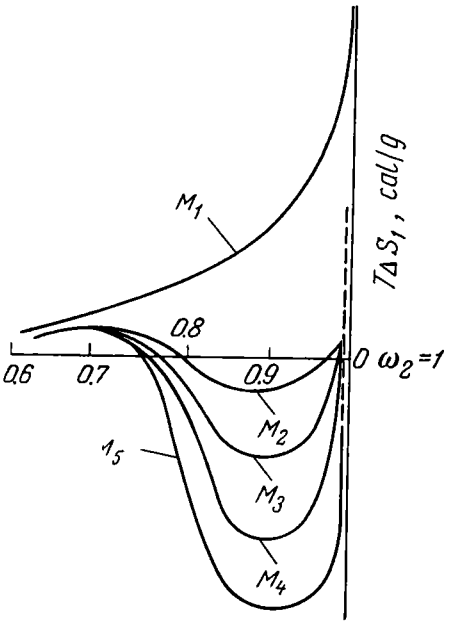

Fig. 13.21. Effect of the molecular mass on entropy of mixing (scheme); $M_1 < M_2 < M_3 < M_4 < M_5$

13.17. THERMODYNAMICS OF SWELLING OF CROSSLINKED POLYMERS

Spatially crosslinked polymers do not dissolve; therefore, the osmotic pressure method cannot be used for determining the thermodynamic affinity of these polymers to a solvent, and the second Virial coefficient. Swelling pressure may be measured or solvent vapour pressure over the gel formed during swelling may be determined, and swelling pressure may be calculated by the following equation:

$$\pi_{swell} = -\frac{1}{\overline{V}_1} RT \ln \frac{p_1}{p_1^0} \qquad (13.93)$$

where $\overline{V}_1$ = partial molar volume of a solvent

$\frac{p_1}{p_1^0}$ = relative pressure of its vapour.

Swelling pressure is determined in special instruments under the conditions of bulk compression, and an experiment is carried out so that external pressure always compensates for swelling pressure. Figure 13.22 shows typical concentration dependence of the swelling pressure of vulcanizates of natural rubber in different

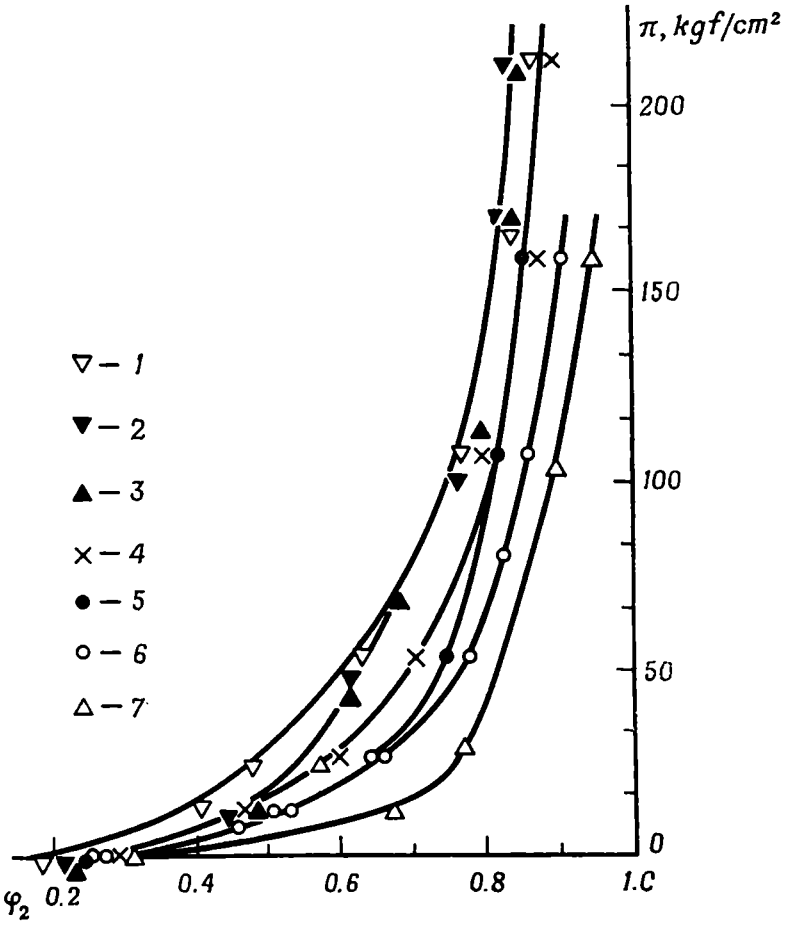

Fig. 13.22. Concentration dependence of swelling pressure of natural rubber in different solvents

solvents. Apparently, these quantities may attain hundreds of atmospheres when polymer concentration in a gel is large. On dilution, swelling pressure diminishes to atmospheric pressure at an equilibrium degree of swelling φ_2^{equil}. Depending on the nature of a solvent, the swelling pressure of equally concentrated gels may differ by 100-160 atm, i.e., it is a very sensitive characteristic of the thermodynamic affinity of a polymer to a solvent.

Figure 13.23 shows the concentration dependence of swelling pressure which has been measured under the conditions of bulk compression and calculated by Eq. (13.93). In the region of not very large values of swelling pressure, these quantities coincide;

in the region of large values, the directly measured swelling pressure is greater than those calculated on the basis of the data on solvent vapour pressure.

The values of swelling pressure thus obtained may be substituted in equation $\Delta\mu_1 = -\pi_{swell}\bar{V}_1$, and $\Delta\mu_2$ and the free energy of mixing may be calculated in a way shown on page 389. In this case, the free energy of mixing which has been determined on the basis of the data of directly measured swelling pressure ΔG_I is

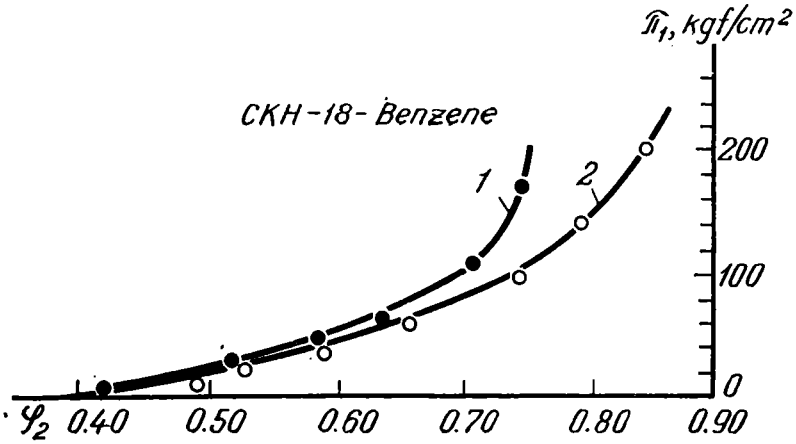

Fig. 13.23. Dependence of swelling pressure on the volume fraction of polymer in a swollen vulcanizate of natural rubber:
1—directly measured; *2*—calculated from sorption data

always more negative than ΔG_{II}, which has been calculated by the data obtained in measuring the solvent vapour pressure over a gel.

This difference is connected with the different conditions of an experiment and with the specific thermodynamics of swelling of network polymers.

Unlike linear polymers, crosslinked polymers undergo highly elastic deformations during swelling. Therefore, changes in free energy originate from the free energy of mixing and that of highly elastic deformation:

$$\Delta G = \Delta G^m + \Delta G^{el} \qquad (13.94)$$

Since chain sections between crosslink points straighten out during elastic deformation and the probability of random unit arrangement decreases, entropy decreases and the term ΔG^{el} enters the equation with a positive sign.

Under the conditions of measurement of solvent vapour pressure over a gel, the latter is in a free state, and elastic deformation is manifested. Under the conditions of bulk compression, when swelling pressure is measured, elastic deformation cannot be manifested, since the specimen cannot expand. Therefore, $\Delta G_{II} < \Delta G_I$.

The difference between them is equal to the work of highly elastic deformation. If it is taken into account, then

$$\Delta G_{II} = \Delta G_{I} \tag{13.95}$$

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CHAPTER 14

Theory of Polymer Solutions

14.1. BASIC CONCEPTS OF THEORY OF SOLUTIONS

In theoretical calculations of the thermodynamic properties of liquids and liquid solutions one is usually interested in what is known as their *configurational* properties, i.e., those that depend only on intermolecular interaction. Internal movement in molecules and atoms is not taken into account. Thus, configurational or intermolecular energy is the energy of a liquid minus the energy of the same substance in the state of an ideal gas at the same temperature. The quantity U_{conf} is negative and equal to the energy of evaporation of the liquid with the opposite sign, i.e., $\lambda - RT$, where λ is the heat of evaporation. Some configurational thermodynamic properties fall into combinatorial and noncombinatorial properties.

Entropy of mixing due only to rearrangement of different molecules is called the *geometrical*, or *combinatorial entropy of mixing*. There is also a *nongeometrical* (*noncombinatorial*) contribution to the entropy of mixing, due to energy interaction between the components in the solution, resulting in contraction of the solvent and the formation of oriented solvate layers. This involves a decrease in entropy of the solvent. If the former contribution $(\Delta S^{M}_{comb} > 0)$ favours dissolution (the term ΔG in the equation $\Delta G = \Delta H - T\Delta S$ becomes more negative), the latter contribution $(\Delta S^{M}_{noncomb} < 0)$ does not favour dissolving. In some systems the first contribution may predominate over the second under certain conditions, and then the total entropy of mixing becomes negative $(\Delta S^{M} < 0)$.

In accordance with this the Gibbs free energy of mixing may be divided into two parts: the combinatorial part, depending on the combinatorial entropy of mixing, and the noncombinatorial part, equal to $\Delta H - T\Delta S_{noncomb}$. If $\Delta S_{noncomb}=0$, then $\Delta G_{noncomb}=\Delta H$.

To derive theoretical equations relating thermodynamic parameters to molecular constants it is necessary to proceed from some solution model. The simplest model is that of the ideal solution, which is a solution consisting of substances whose molecules are identical in chemical constitution and size.

Ideal Solution. When an ideal solution forms, the heat of solution equals zero because the energy of interaction between all molecules is the same. Hence, molecular distribution is due only to thermal motion, and therefore the equation derived by Gibbs for mixtures of ideal gases may be used for the entropy of mixing. The derivation of this equation is based on the assumption of random arrangement of molecules. In this case the entropy of mixing is equal to the difference between the entropy of the mixture and the sum of entropies of the components, i.e., for a binary ideal solution

$$\Delta S_{mix} = S_{sol} - (S_1^0 + S_2^0) = k \ln W - k(\ln W_1^0 + \ln W_2^0) \quad (14.1)$$

where W, W_1^0, and W_2^0 are the numbers of possible arrangements of molecules in the mixture and in the pure components.

The number of possible arrangements of molecules or the *thermodynamic probability* of a system consisting of x_1 molecules of kind I is equal to the number of their permutations, i.e., $x_1!$. Similarly, the number of possible arrangements of x_2 molecules of kind II is $x_2!$, and the number of possible arrangements of molecules in the mixture is $(x_1 + x_2)!$. Hence,

$$\Delta S_{mix} = k \ln (x_1 + x_2)! - k(\ln x_1! + \ln x_2!)$$

or

$$\Delta S_{mix} = k \ln \frac{(x_1 + x_2)!}{x_1! + x_2!} \quad (14.2)$$

According to Stirling's formula, which is valid for large N values, $\ln N! \approx N \ln N - N$, and therefore

$$\Delta S_{mix} = k[(x_1 + x_2) \ln (x_1 + x_2) - x_1 - x_2 - x_1 \ln x_1 + x_1 - x_2 \ln x_2 + x_2]$$

whence

$$\Delta S_{mix} = -k\left[x_1 \ln \frac{x_1}{x_1 + x_2} + x_2 \ln \frac{x_2}{x_1 + x_2}\right]$$

Here

$$\frac{x_1}{x_1 + x_2} = N_1; \quad \frac{x_2}{x_1 + x_2} = N_2$$

where N_1 and N_2 are the mole fractions of the components. Then

$$\Delta S_{mix} = -k(x_1 \ln N_1 + x_2 \ln N_2) \quad (14.3)$$

Dividing and multiplying the right side of Eq. (14.3) by Avogadro's number, we get

$$\Delta S_{mix} = -kN_A\left(\frac{x_1}{N_A}\ln N_1 + \frac{x_2}{N_A}\ln N_2\right)$$

where $kN_A = R$, and the ratios x_1/N_A and x_2/N_A are the numbers of moles of the components n_1 and n_2. Thus, the entropy of mixing of two ideal gases, or the *ideal entropy of mixing*

$$\Delta S_{mix} = -R(n_1 \ln N_1 + n_2 \ln N_2) \qquad (14.4)$$

For one mole of an ideal mixture $n_1 = N_1$ and $n_2 = N_2$. Hence,

$$\Delta S_{mix} = -R(N_1 \ln N_1 + N_2 \ln N_2) \qquad (14.5)$$

Equation (14.5) can be used for calculating the entropy of mixing of two liquids forming an ideal solution. In this case $S^E = 0$.

The ideal solution model does not correspond to real solutions. Therefore, to calculate the thermodynamic functions of real solutions more complex models must be used. Some of them are examined briefly below.

Regular Solution. The term regular solution was introduced by Hildebrand to denote a solution, on formation of which $\Delta H \neq 0$ and in which the molecules of the mixed components are arranged like in an ideal solution, i.e., absolutely at random. This means that the entropy of mixing equals the ideal entropy of mixing ($\Delta S_{mix} = \Delta S_{id}$; $S^E = 0$).

It is assumed that in a binary solution the molecules X_1 and X_2 of the components of the first and second kinds can form the pairs X_1X_1, X_2X_2, and X_1X_2 with the energies of interaction E_{11}, E_{22}, and E_{12}, respectively.

It is also assumed that the energy of interaction of the molecules in the liquid is proportional to the energy of vaporization of the liquid.

It can be shown that if the molecules of the mixed components are close in size, the change in internal energy of a component on formation of a mole of a regular solution is

$$\Delta U_1 = U_1 - U_1^0 = [(\Delta E_1^0)^{1/2} - (\Delta E_2^0)^{1/2}]^2 N_2^2 \qquad (14.6)$$

where U_1 = partial molar internal energy of first component in solution

U_1^0 = molar internal energy of first component before mixing

N_2 = mole fraction of second component

(ΔE_1^0) and (ΔE_2^0) = energy of vaporization of a mole of first and second components, respectively.

For solutions in which the component molecules differ in size the expression for the change in internal energy of the first component has the form

$$U_1 - U_1^0 = V_1\varphi_2^2\left[\left(\frac{\Delta E_1^0}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^0}{V_2}\right)^{1/2}\right]^2 \qquad (14.7)$$

where V_1 and V_2 = partial molar volumes of components
φ_2 = volume fraction of second component.

The ratio $\Delta E_i^0/V_i$ is called the energy density of molecular attraction, or the *cohesive energy density* (*c.e.d.*) of the component in question, and the quantity $(\Delta E_i^0/V)^{1/2}$ is known as the *solubility parameter* (denoted by δ).

The square of the quantity in brackets in Eq. (14.7), characterizing the interaction between the molecules, is denoted by B:

$$B = \left[\left(\frac{\Delta E_1^0}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2^0}{V_2}\right)^{1/2}\right] = (\delta_1 - \delta_2)^2 \qquad (14.8)$$

Volume changes in condensed systems are usually very small and therefore the change in internal energy is usually supposed to be equal to the change in enthalpy, i.e. for the first component

$$\Delta H_1 = \Delta U_1 = BV_1\varphi_2^2 \qquad (14.9)$$

and for the second component

$$\Delta H_2 = BV_2\varphi_1^2 \qquad (14.10)$$

The difference of chemical potentials of the component is expressed by the equation

$$\Delta\mu_i = \Delta H_i - T\,\Delta S_{i\,id} = RT\ln N_i + V_1\varphi_2^2(\delta_1 - \delta_2) \qquad (14.11)$$

Actually, as was shown on p. 402, $\Delta H_V \neq \Delta U_p$, and therefore the calculated values of $(\Delta U)_V$ should be substituted into Eq. (14.9) through (14.11).

All the equations given above lend themselves to experimental verification, because the energy of vaporization can easily be determined. However, the theory of regular solutions itself is built on the incorrect assumption that the arrangement of molecules in a solution is independent of the heat effect of dilution; absolutely random distribution of molecules is possible only if the heat effect of dilution is zero. Generation or absorption of heat always involves predominant groupings of molecules in the solution, which excludes random distribution. In the presence of a heat effect the entropy of mixing should differ from its ideal value. Hence the applicability of the theory of regular solutions is limited since it is valid only for weakly polar and nonpolar molecules possessing spherical symmetry.

Lattice Models of Solutions. In the thirties most theories of solutions were based on the idea of quasicrystalline structure of liquids and liquid solutions. One of them is the theory of "strictly regular solutions" developed by Guggenheim for molecular mixtures of nonpolar and weakly polar liquids.

The theory of strictly regular solutions is based on the following assumptions:

1. A solution has a quasicrystalline lattice with the coordination number Z.
2. Each molecule occupies one site in the lattice and hence the molecules of the components should be of approximately the same size and shape.
3. Only nearest neighbours interact.
4. Molecules move relative to their equilibrium positions in the lattice cell, and their movement does not change on mixing.

A very important conclusion follows from these assumptions: mixing involves a zero change in volume, and the effect of this change on the heat and entropy of mixing may be neglected.

As Hildebrand noted despite the resemblance of terms the concepts "strictly regular" and "regular" solutions are directly opposite. The regular solution model assumes complete disorder in distribution of molecules, whereas the strictly regular solution model assumes complete order.

In the theory of strictly regular solutions the most important parameter characterizing the system quantitatively is the *interchange energy*, equal to the algebraic sum of energies of contacts of pairs 1-2, 1-1, 2-2:

$$\Delta\omega = \omega_{1,2} - \frac{1}{2}(\omega_{1,1} - \omega_{2,2}) \qquad (14.12)$$

If the interchange energy is zero, the system is athermal, and if it differs from zero, the system is not athermal.

If the molecules of both components of an athermal mixture are of the same size, the entropy of mixing should be equal to its ideal value.

If the component molecules of an athermal mixture differ greatly in size (polymer solutions), the entropy of mixing is not equal to its ideal value.

14.2. POLYMER SOLUTIONS. FLORY-HUGGINS THEORY

14.2.1. Entropy of Mixing on Formation of an Athermal Solution

Depending on the chemical constitution of the polymer and solvent molecules, solutions of macromolecular compounds, like solutions of low-molecular substances, may be divided into classes

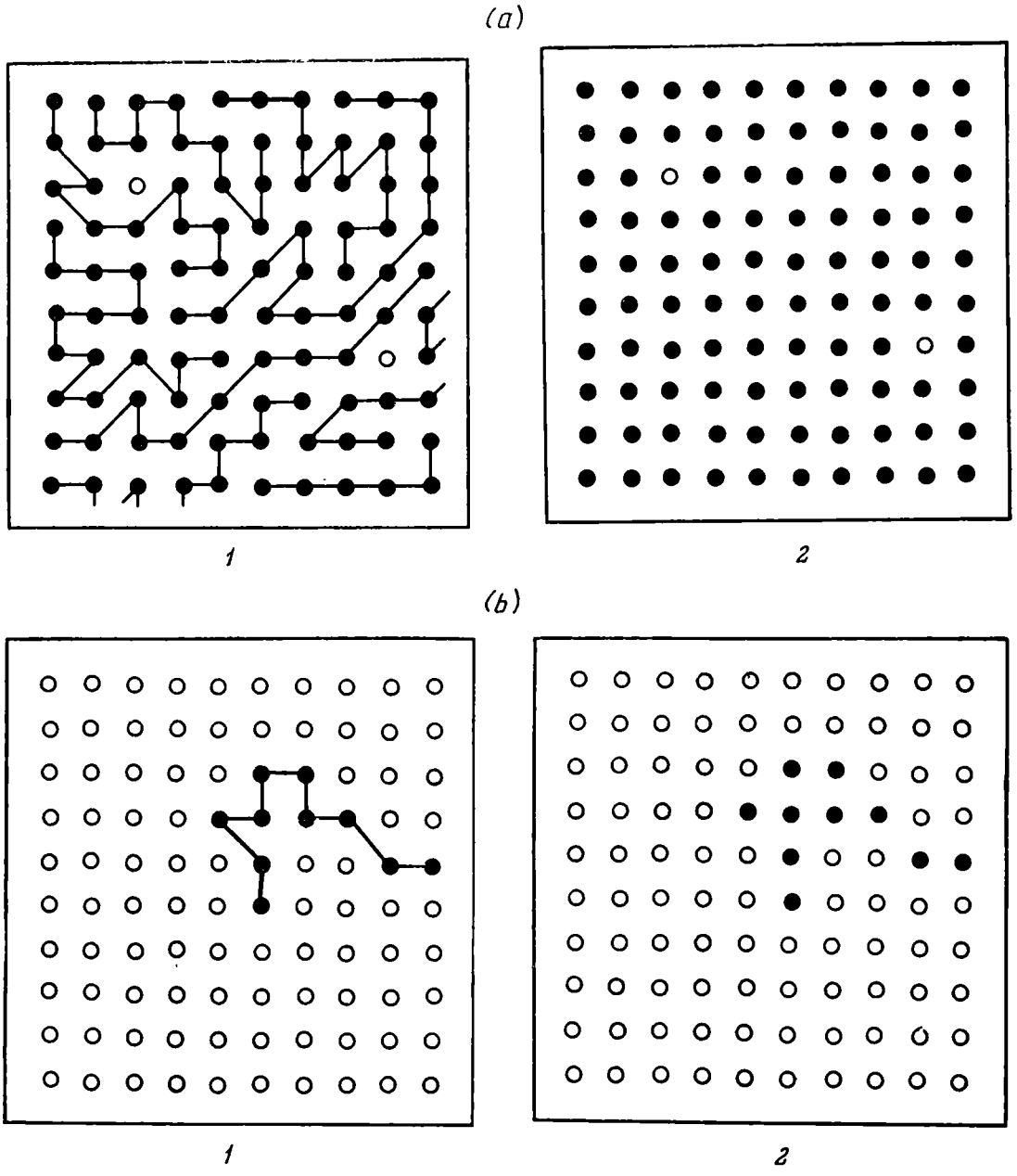

Fig. 14.1. Model of quasicrystalline lattice:
a — at low solvent concentrations; *b* — at high solvent concentrations; *1* — black spheres connected into chains; *2* — free black spheres

in which the orientation of the molecules is not essential and in which molecular orientation plays an important part. Obviously, systems of the former class are the simpler ones, and the simplest of them is the athermal system.

For this reason the first theoretical calculations carried out independently by Flory and by Huggins were made for athermal mixing of a polymer with a low-molecular liquid.

Both authors proceeded from the quasicrystalline solution model shown schematically in Fig. 14.1. The white circles represent solvent molecules and the black ones, polymer chain segments tied with chemical bonds or molecules of hydrogenated monomers with no chemical bonds between them. It is assumed that solvent molecules can exchange sites with hydrogenated monomer molecules and with polymer chain segments. The latter is possible only if the chain is capable of bending. An exchange of sites between unlike molecules results in an increase in the number of ways they can be arranged (thermodynamic probability), and hence, in an increase of entropy. Obviously, the entropy of mixing should depend on the presence or absence of bonds between the segments, and also on the concentration of the solution.

At low solvent concentrations (initial stage of dissolving or swelling) the number of ways of arranging the white circles is the same in both cases, because the white spheres can occupy any site whatsoever by exchanging places with the black circles. At higher solvent concentrations the number of ways of arranging the white circles in the system is larger if the black circles are not linked to one another, since the chemical bonds between the segments limit the possibility of exchange (Fig. 14.1*b*). This qualitative treatment of solutions, given by Meyer, forms the basis of Flory's and Huggins' theoretical calculations.

These calculations involved the following assumptions:

1. All polymer molecules are flexible and identical in size *.
2. The quasicrystalline lattice consists of n_0 sites, each containing one solvent molecule or one solute submolecule (chain segment) capable of exchanging places with the solvent molecules, and $\Delta H = 0$.
3. The system contains n solvent molecules and N chains, each chain consisting of r segments. Hence, $n_0 = rN + n$.
4. The coordination number of the lattice is Z. If a chain segment is situated in a definite site, Z indicates the number of neighbouring sites in which the next chain segment can be placed.

The method of counting the number of possible conformations the chain can assume consists in filling the lattice by successively placing new polymer chain segments on it.

Assuming that N polymer chains or an equivalent number of solvent molecules are already contained in the lattice, there are $(n_0 - rN)$ unoccupied sites left, and hence, the first segment of the $(N + 1)$th chain can be arranged in $(n_0 - rN)$ ways. If the lattice were emtpy, the second segment, provided the first segment were fixed, could be placed in Z ways. Since part of the sites is

* In subsequent papers Flory showed this calculation to be valid for a polydisperse polymer as well.

occupied, the actual number of possible arrangements is as many times smaller than this as the number of unoccupied sites is smaller than the total number of sites. In other words, the number of ways of arrangement of the second segment equals

$$\frac{Z(n_0 - rN)}{n_0} \tag{14.13}$$

The number of possible ways of arrangement of the third chain segment is

$$\frac{(Z-1)(n_0 - rN)}{n_0} \tag{14.14}$$

The authors take the number of possible arrangements of each subsequent segment to be equal to that calculated from Eq. (14.14). Then the number of possible conformations ν_{N+1}, which can be assumed by one chain consisting of r segments, is equal to

$$\nu_{N+1} = \frac{1}{2} \frac{(n_0 - rN)\, Z\, (n_0 - rN)\, (Z-1)^{r-2}\, (n_0 - rN)^{r-2}}{n_0 n_0^{r-2}} \tag{14.15}$$

The factor 1/2 is introduced into Eq. (14.15) because the chain has two ends, either of which can be the first segment placed on the lattice. For this reason if calculated without the factor 1/2 the number of possible conformations assumed by the chain would be twice as high as it should be.

After simplifying expression (14.15) becomes

$$\nu_{N+1} = \frac{1}{2} (Z-1)^{r-1} (n_0 - rN)^r n_0^{1-r} \tag{14.16}$$

The thermodynamic probability W of the solution can be calculated as the product of the number of ways of arranging all the N chains and all the solvent molecules. In doing so only permutations of solvent molecules and polymer chains with each other are of importance. Permutations between polymer chains or between solvent molecules give no new ways of arrangement Therefore the product $\prod_{N=1}^{N} \nu_N$ should be divided by the number of permutations of like molecules, which equals $N!$. Thus,

$$W = \frac{1}{N!} \prod_{N=1}^{N} \nu_N \tag{14.17}$$

Substituting into Eq. (14.17) the value of ν_N corresponding to Eq. (14.16), applying Stirling's formula and making a number of transformations, we get the expression

$$W = \left(\frac{Z-1}{e}\right)^{(r-1)N} \left(\frac{1}{2}\right)^N \frac{(n + rN)^{n+N}}{n^n (rN)^N} \tag{14.18}$$

According to Boltzmann's equation, taking the logarithm of Eq. (14.18) yields

$$S = k \ln W = -k \left(n \ln \frac{n}{n + rN} + N \ln \frac{Nr}{n + rN} \right) + \\ + k(r - 1) N [\ln (Z - 1) - 1] - kN \ln 2 \qquad (14.19)$$

Expression (14.19) is the entropy of the solution, S_{sol}. The entropy of mixing equals

$$\Delta S_{mix} = S_{sol} - (S_{polym} + S_{solv}) \qquad (14.20)$$

Suppose that the initial components are in an ideal crystalline state, i.e., that $S_{polym} \approx 0$ and $S_{solv} \approx 0$. Then the entropy of mixing ΔS_{mix} will be equal to the entropy of the solution S_{sol}. If the initial components are not in the crystalline, but in the liquid state, it is necessary to calculate the entropy of transition from the crystalline to the liquid state, known as the *entropy of disorientation* of the polymer, ΔS^*.

The disorientation entropy is the difference between the entropies of the substance in the amorphous and crystalline states. The latter is zero, but the entropy of the amorphous substance is calculated from Eq. (14.19) on the assumption that the lattice contains either only polymer chains ($n = 0$), or only solvent molecules ($N = 0$). Under these conditions

$$\Delta S^* = k(r - 1) N [\ln (Z - 1) - 1] - kN \ln 2 \qquad (14.21)$$

The entropy of mixing of a polymer with a solvent equals

$$\Delta S_{mix} = S - \Delta S^*$$

Subtracting Eq. (14.21) from Eq. (14.19), we obtain

$$S_{mix} = -k \left(n \ln \frac{n}{n + rN} + N \ln \frac{Nr}{n + rN} \right) \qquad (14.22)$$

The ratios $n/(n + rN)$ and $Nr/(n + rN)$ are called the volume fractions of solvent and a polymer, respectively; denoting them by φ_1 and φ_2, Eq. (14.22) can be rewritten as

$$\Delta S_{mix} = -k (n \ln \varphi_1 + N \ln \varphi_2) = -R (n_1 \ln \varphi_1 + n_2 \ln \varphi_2) \qquad (14.23)$$

where n_1 and n_2 are the numbers of moles of the components.

Equation (14.23) differs from Eq. (14.4) in that it contains volume instead of mole fractions of the components.

The partial entropies of mixing of the components can be found from Eq. (14.22):

$$\Delta S_1 = \frac{\partial (\Delta S)}{\partial n} = -R \ln (1 - \varphi_2) - R \left(1 - \frac{1}{r} \right) \varphi_2 \qquad (14.24)$$

and

$$\Delta S_2 = \frac{\partial (\Delta S)}{\partial N} = -R \ln (1 - \varphi_1) + R (r - 1) \varphi_1 \qquad (14.25)$$

14.2.2. Change in Gibbs Free Energy on Dissolution of Polymers

Flory's and Huggins' calculation was made for athermal mixing ($\Delta H = 0$). Accordingly, the change in the Gibbs free energy of the solution is expressed by the equation

$$\Delta G = -T\Delta S_{mix} = RT(n_1 \ln \varphi_1 + n_2 \ln \varphi_2) \qquad (14.26)$$

The authors of the theory believe that the equation derived by them for the entropy of mixing is also applicable to nonathermic processes of mixing. Therefore, to express the difference of chemical potentials they use the basic thermodynamic relation $\Delta\mu_i = \Delta H_i - T\Delta S_i$, substituting the value of ΔS_i from Eq. (14.24) and the values of ΔH_i from Eqs. (14.9) and (14.10). This results in the following equations:

$$\Delta\mu_1 = RT \ln(1 - \varphi_2) + RT\left(1 - \frac{1}{r}\right)\varphi_2 + BV_1\varphi_2^2 \qquad (14.27)$$

$$\Delta\mu_2 = RT \ln(1 - \varphi_1) - RT(r - 1)\varphi_1 + BV_2 r\varphi_1^2 \qquad (14.28)$$

The parameter B has the same meaning as in Eq. (14.8), i.e., it is the parameter of energy interaction of the components.

Huggins derived the following equations for the activities of the components:

$$\ln a_1 = \ln \varphi_1 + \left(1 - \frac{V_1}{V_2}\right)\varphi_2 + \chi_1\varphi_2^2 \qquad (14.29)$$

and

$$\ln a_2 = \ln \varphi_2 + \left(1 - \frac{V_2}{V_1}\right)\varphi_1 + \chi_2\varphi_1^2 \qquad (14.30)$$

where a_1 and a_2 = activities of a solvent and a polymer
φ_1 and φ_2 = their volume fractions
V_1 and V_2 = their partial volumes in solution
χ_1 and χ_2 = empirical constants allowing for the heat of mixing and deviations from absolute disorder (Huggins constants)*.

Since the polymer molecule consists of r segments, the volume of each of which is taken in the theory to be equal to the volume of one solvent molecule, the volume of a mole of a polymer is r times larger than that of a solvent, i.e., $V_2 = V_1 r$. Hence,

$$\frac{1}{r} = \frac{V_1}{V_2} \qquad (14.31)$$

* In early papers on the thermodynamics of polymer solutions Huggins constants were denoted by μ. At present the letter χ is more commonly used.

Taking into account the relation $\Delta\mu_1 = RT \ln a_1$ and substituting expression (14.31) into Eq. (14.29), we get Eq. (14.27). Hence, it follows that

$$\chi_1 = \frac{BV_1}{RT} = \frac{(\delta_1 - \delta_2)^2 V_1}{RT} \tag{14.32}$$

For a polymer of very high molecular mass V_1/V_2 is small and may be neglected. Then Eq. (14.29) becomes simpler:

$$\ln a_1 = \frac{\Delta\mu_1}{RT} = \ln(1 - \varphi_2) + \varphi_2 + \chi_1\varphi_2^2 \tag{14.33}$$

Parameter χ_1 plays a very important part in the theory of polymer solutions and is usually regarded as the parameter of interaction between a polymer and a solvent. In this connection one of the problems of theory is to find the quantitative value of parameter χ_1. However, so far it can be determined only experimentally.

Determination of Parameter χ_1 from Relative Vapour Pressure over Solution. Equation (14.33) can be represented as

$$\ln \frac{p_1}{p_1^0} = \ln(1 - \varphi_2) + \varphi_2 + \chi_1\varphi_2^2 \tag{14.34}$$

where p_1/p_1^0 is the relative vapour pressure of a solvent.

Measuring the value p_1/p_1^0 over a wide range of concentrations and plotting $\left(2.303 \log \frac{p_1}{p_1^0(1-\varphi_2)} / \varphi_2\right) - 1$ against the volume fraction of polymer φ_2, we get a straight line, the slope of which is equal to χ_1.

Determination of χ_1 by Osmotic Pressure of Solution. Substituting the value of $\ln a_1$ from Eq. (14.29) into the equation $\pi = -(RT/V_1) \cdot \ln a_1$, we obtain the theoretical equation for the osmotic pressure of polymer solutions in the following form:

$$\pi = -\frac{RT}{V_1} \ln a_1 = -\frac{RT}{V_1} \ln \varphi_1 - \frac{RT}{V_1}\left(1 - \frac{V_1}{V_2}\right)\varphi_2 - \frac{RT}{V_1}\chi_1\varphi_2^2 \tag{14.35}$$

After transformations and replacing volume fractions with concentrations expressed in g/ml ($c_2 = \varphi_2 d_2$) we get the equation

$$\frac{\pi}{c_2} - \frac{RTd_1c_2^2}{3M_1d_2^3} = \frac{RT}{M_2} + \frac{RTd_1}{M_1d_2^2}\left(\frac{1}{2} - \chi_1\right)c_2 \tag{14.36}$$

where d_1 and d_2 = densities of a solvent and a polymer
M_1 and M_2 = their molecular masses.

At low concentrations the second term on the left-hand side of the equation is small and may be neglected. Then Eq. (14.36) becomes Eq. (13.54) of Chap. 13, the graphical representation of

which is a straight line (see Fig. 13.8). The slope of this line equals $\frac{RTd_1}{M_1 d_2^2}\left(\frac{1}{2}-\chi_1\right)$. Hence, it is possible to calculate the second Virial coefficient:

$$A_2=\frac{d_1}{M_1 d_2^2}\left(\frac{1}{2}-\chi_1\right) \tag{14.37}$$

It follows from Eq. (14.32) that χ_1 is a dimensionless parameter equal to the ratio of the energy of interaction of the polymer with the solvent molecules to the kinetic energy RT, which should not depend on the concentration of a solution. This parameter is empirical, and it is determined by the methods expounded on page 429. By comparing Eq. (14.37) with the given one on page 387, it follows that

$$\text{for an ideal solvent } A_2=0;\ \chi_1=\frac{1}{2}$$

$$\text{for good solvents } A_2>0;\ \chi_1<\frac{1}{2}$$

$$\text{for poor solvents } A_2<0;\ \chi_1>\frac{1}{2}$$

Hence, χ_1 is a measure of thermodynamic affinity of a solvent for the polymer, or a measure of the quality of a solvent. The smaller χ_1, the better is the solvent thermodynamically. For very poor solvents, χ_1 may be higher than unity, and for very good ones, χ_1 may be negative.

It follows from a comparison of Eqs. (14.37) and (14.32) that parameter χ_1 is of a dual nature. On the one hand, χ_1 is connected with the density of cohesion energy, i.e., with the internal energy of interaction, and, on the other, it is connected with the second Virial coefficient, which is a measure of thermodynamic affinity and, consequently, depends not only on internal energy, but also on the entropy of mixing. This duality originated, because theory takes account of only the entropy of mixing, which is due to molecular rearrangements, i.e., the combinatorial entropy of mixing (p. 398). At the same time, the noncombinatorial entropy of mixing originates in the presence of the thermal effect; in order to take this entropy into account, Flory later introduced the concept of *residual chemical potential* $\Delta\mu_1^R$ which includes the enthalpy of mixing and the noncombinatorial entropy of mixing:

$$\Delta\mu_1^R=\Delta\bar{H}_1-T\Delta\bar{S}_1^{\text{noncomb}} \tag{14.38}$$

This parameter differs from $\Delta\mu_1$ by the term $T\Delta\bar{S}_1^{\text{comb}}$, which, according to Eq. (14.24), at high values of r is equal to $-RT\,[\ln(1-\varphi_2)+\varphi_2]$.

Hence,

$$\Delta\mu_1 = \Delta\mu_1^R - T\bar{S}_1^{comb} \tag{14.39}$$

and Eq. (14.33) can be written as follows:

$$\frac{\Delta\mu_1^R - T\Delta\bar{S}_1^{comb}}{RT} = -\frac{T\Delta\bar{S}_1^{comb}}{RT} + \chi_1\varphi_2^2 \tag{14.40}$$

Whence,

$$\chi \equiv \frac{\Delta\mu_1^R}{RT\varphi_2^2} = \frac{\Delta\bar{H}_1}{RT\varphi_2^2} - \frac{\Delta\bar{S}_1^{noncomb}}{R\varphi_2^2} \tag{14.41}$$

Flory designated the first term of Eq. (14.41), which depends only on the enthalpy of mixing, by χ_H, and the second term, which is determined by the noncombinatorial entropy of mixing, by χ_S

$$\chi_H = \frac{\Delta\bar{H}_1}{RT\varphi_2^2}; \quad \chi_S = -\frac{\Delta\bar{S}_1^{noncomb}}{R\varphi^2} \tag{14.42}$$

The total value is equal to their sum:

$$\chi_1 = \chi_H + \chi_S$$

14.2.3. Phase Equilibrium in Polymer Solutions

When coexisting phases are in equilibrium, the chemical potentials of both components in both phases should be equal (the superscripts I and II indicate the first and second phases):

$$\begin{aligned} \Delta\mu_1^I &= \Delta\mu_1^{II} \\ \Delta\mu_2^I &= \Delta\mu_2^{II} \end{aligned} \tag{14.43}$$

If mixing of a polymer with a solvent occurs athermally ($\Delta H_1 = 0$), then B in Eq. (14.9) equals zero. Analysis of Eq. (14.27) shows that the quantity $\Delta\mu_1 = 0$ when $\varphi_2 = 0$ and $\Delta\mu_1 \to \to -\infty$ when $\varphi_2 \to 1$. Hence, for an athermal mixture, as could be expected, as the concentration of the solution changes from a pure solvent to a pure polymer, $\Delta\mu_1$ varies from zero to minus infinity, i.e., the components are completely miscible over the whole range of compositions.

If $B \neq 0$, then with φ_2 changing from 0 to 1 all the three terms on the right side of Eq. (14.27) vary so that a maximum and a minimum appear on the $\Delta\mu$ vs. φ_2 curve.

At concentrations corresponding to the extreme points condition (14.43) is observed, i.e., the solution separates into two phases.

To determine the conditions of phase separation it is obviously necessary to differentiate Eq. (14.27) with respect to φ_2 and equate

$\partial\Delta\mu_1/\partial\varphi_2$ to zero. After appropriate transformations we arrive at the following expressions for the critical concentration:

$$\varphi_{2\,cr} = \frac{1}{1+\sqrt{r}} \tag{14.44}$$

and for the critical temperature,

$$T_{cr} = \frac{BV_1 r}{R(1+\sqrt{r})^2} \tag{14.45}$$

and for critical value of the parameter of interaction

$$\chi_{1\,cr} = \frac{(1+r^{1/2})^2}{2r} = \frac{1}{2r} + \frac{1}{r^{1/2}} + \frac{1}{2} \tag{14.46}$$

It follows from Eq. (14.44) that the larger the value of r, the smaller will $\varphi_{2\,cr}$ be, i.e., at high r values phase separation begins at low polymer concentrations in the solution. For example, if the molecular mass of the polymer is 10^6 ($r \approx 10^4$), $\varphi_{2\,cr} \approx 0.01$. Thus, theory predicts separation of nonathermal polymer-solvent systems for polymers of high molecular mass.

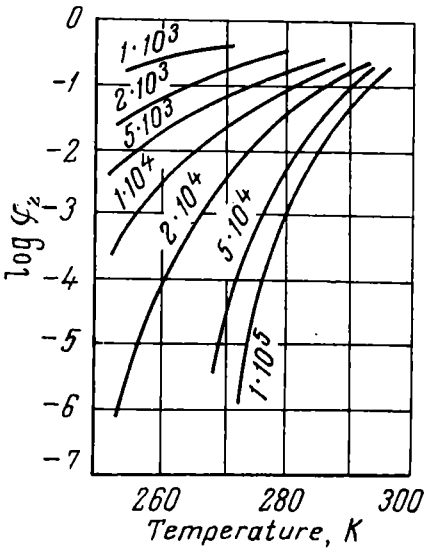

Fig. 14.2. Solubility of natural rubber in benzene at various temperatures. The numbers on the curves are molecular masses of natural rubber

At the critical temperature of dilution the composition of the coexisting phases is the same. But on cooling the composition of the phases changes with temperature, and the higher the molecular mass of a polymer, the sharper this change (Fig. 14.2). It is evident from the figure that with a comparatively small change in temperature the volume fraction of a polymer in a given phase may become very small. The phase coexisting with it will then be a swollen polymer with a high φ_2 value. The theoretical propositions discussed above can be placed at the basis of the theory of fractionation, i.e., separation of a polymer into fractions of close molecular masses (Chap. 12). It follows from Eq. (14.45) that the critical temperature of mixture of polymer-homologues depends on their molecular mass (the value of r). Hence, on variation of the temperature of a solution of an unfractionated polymer, fractions of given molecular mass should precipitate out at values of $T = T_{cr}$. Thus, it is possible, in principle, to fractionate a polymer by cooling its solution in some liquid. As was pointed out in Chapter 12, accomplishment of this method

however involves great difficulties. The temperature coefficient of solubility of high-molecular polymers is very high, i.e., a sharp change in composition of a phase corresponds to a change in temperature of only a few degrees (see Fig. 14.2). This means that the polymer is either completely miscible with the liquid in question, or does not dissolve in it at all. A temperature range wherein the polymer and low-molecular liquid are partially miscible can be observed only in a few cases. For this reason individual liquids are practically not used for fractionation. Polymers are fractionated at constant temperature by adding a nonsolvent to the polymer solution until the latter becomes turbid. All the above theoretical reasoning remains valid with the only exception that in such fractionation the phases differ not only in volume fractions of a polymer, but also in ratio of the liquids used.

14.2.4. Theory of Dilute Polymer Solutions

For very dilute solutions the equations can be simplified. Thus, expanding the term ln $(1-\varphi_2)$ of Eq. (14.24) in a series and retaining the first two terms of the series, we obtain

$$\Delta\bar{S}_1 = -R\left(-\frac{\varphi_2^2}{2}-\frac{\varphi_2}{r}\right) \tag{14.47}$$

At high r values the last term of this equation may be neglected, and then

$$\Delta\bar{S}_1 = R\frac{\varphi_2^2}{2} \tag{14.48}$$

Since the partial entropy of mixing differs in different solvents, factor ψ_1 is introduced to take into account the effect of the nature of a solvent on the entropy of mixing. This results in

$$\Delta\bar{S} = R\psi_1\varphi_2^2 \tag{14.49}$$

It follows from Eqs. (14.9) and (14.32) that

$$\Delta\bar{H}_1 = RTk_1\psi_2^2 \tag{14.50}$$

where $k_1 = \chi_1$ is a constant which takes into account the energy of interaction of the polymer-solvent system.

Substituting the value of $\Delta\bar{H}_1$ from Eq. (14.50) and the value of $\Delta\bar{S}_1$ from Eq. (14.49) into the equation $\Delta\mu_1 = \Delta\bar{H}_1 - T\Delta\bar{S}_1$, we get

$$\Delta\mu_1 = RT(k_1-\psi_1)\varphi_2^2 \tag{14.51}$$

If we introduce the values of $\Delta\bar{H}_1 = R + \chi_H\varphi_2^2$ and $\Delta\bar{S}_1 = \frac{R\varphi_2^2}{2}$ into the expression $\Delta\mu_1 = \Delta\bar{H}_1 - T\Delta\bar{S}_1$, we shall obtain

$$\Delta\mu_1 = RT\left(\chi_H - \frac{1}{2}\right)\varphi_2^2 \tag{14.52}$$

whence

$$\chi_H - \frac{1}{2} = k_1 - \psi_1 \tag{14.53}$$

If the parameter θ, determined by the relation

$$\theta = \frac{k_1 T}{\psi_1} \tag{14.54}$$

is introduced, Eq. (14.51) becomes

$$\Delta\mu_1 = -RT\psi_1\left(1 - \frac{\theta}{T}\right)\varphi_2^2 \tag{14.55}$$

It follows from Eqs. (14.54) and (14.55) that θ has the dimension of temperature. The physical sense of this temperature, known as the *Flory temperature*, can be demonstrated as follows:

(a) For an ideal solution $\Delta\mu_1 = RT \ln N_1$. If the ideal solution is very dilute, then $N_1 \to 1$ and $\ln N_1 \to 0$, therefore $\Delta\mu_1 \to 0$. It follows from Eq. (14.55) that this is possible when $\theta = T$. Thus, the Flory temperature is the temperature whereat no deviations from ideality are observed in dilute polymer solutions.

(b) In ideal dilute solutions the osmotic pressure $\pi = RTc_2$ [Eq. (13.54), Chap. 13], or $\frac{\pi}{c_2} = RT$. Hence, the second Virial coefficient equals zero.

Thus, the Flory temperature is the temperature at which the second Virial coefficient becomes zero.

(c) From Eqs. (14.53) and (14.54), we can obtain an equation which connects θ-temperature with the critical value of $\chi_{1\,cr}$

$$\chi_{1\,cr} = \frac{1}{2} - \psi_1\left(1 - \frac{\theta}{T_{cr}}\right) \tag{14.56}$$

Substituting the value of $\chi_{1\,cr}$ from Eq. (14.46) in Eq. (14.56), we obtain

$$\frac{(1+\sqrt{r})^2}{2r} = \frac{1}{2} - \psi_1\left(1 - \frac{\theta}{T_{cr}}\right) \tag{14.57}$$

Whence,

$$\frac{1}{T_{cr}} = \frac{1}{\theta} + \frac{1}{\theta}\cdot\frac{1}{\psi_1}\left(\frac{1}{\sqrt{r}} + \frac{1}{2r}\right) \tag{14.58}$$

The number of segments in chain r is proportional to the molecular mass of polymer M. Therefore, Eq. (14. 58) can be rewritten as follows:

$$\frac{1}{T_{cr}} = \frac{1}{\theta} + K \cdot \frac{1}{\sqrt{M}} \qquad (14.59)$$

where K = proportionality factor.

It follows from the equation that at $T = \theta$ $M \to \infty$, i.e., $\frac{1}{\sqrt{M}} \to 0$. Thus, θ-temperature is the critical temperature of dilution of a polymer of an infiinitely large molecular mass. Evidently, when the temperature is higher, all members of a given polymer homologous series infinitely mix together with a given solvent.

Hence, θ-temperature can be determined by measuring the second Virial coefficient at different temperatures, extrapolating the linear dependence obtained to $A_2 = 0$ (straight line, Fig. 14.3), or, when the critical temperature of mixing of various fractions of a polymer in a certain solvent is to be determined, extrapolating the linear dependence $\frac{1}{T_{cr}} = f\left(\frac{1}{\sqrt{M}}\right)$ to $\frac{1}{\sqrt{M}} = 0$ (straight line *1*, Fig. 14.3).

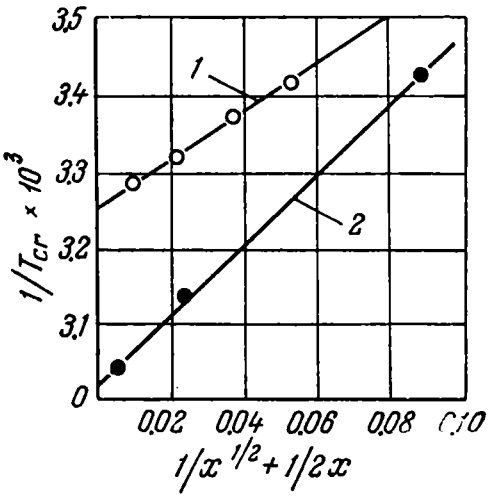

Fig. 14.3. Dependence of inverse critical temperature of phase separation on molecular mass:
1—solution of polystyrene in cyclohexane; *2*—solution of polyisobutylene in diisobutyl ketone

These relations are of such a form for systems with UCST. If a system has LCST, the relations $A_2 = f(T)$ and $\frac{1}{T_{cr}} = f\left(\frac{1}{\sqrt{M}}\right)$ are expressed by curve *2* in Fig. 14.3, i.e., A_2 decreases as temperature rises, and T_{cr} decreases as molecular mass grows. In extrapolating these straight lines, we obtain the value of the second θ-temperature, which is known as the Rowlinson temperature. If a system has UCST and LCST, it should have two θ-temperatures, and this is observed.

It should be noted that the values of θ-temperature obtained for the same system from the data on temperature dependence of A_2 and those obtained from the data on the dependence of T_{cr} of a solution on the molecular mass of the polymer do not always coincide.

The theory of dilute polymer solutions makes it possible to relate certain thermodynamic characteristics of the solution to the size of the coils formed by flexible chains.

In very dilute solutions, when there is no interaction between polymer chains, the latter may be regarded as isolated formations. Such an isolated flexible chain tends to coil up, the size of the coil being determined experimentally and calculated theoretically.

Calculation of coil size reduces to determining the root-mean-square end-to-end distance by the formulas given in Chap. 4. The coil sizes found from light scattering data (Chap. 16) are however much larger than those calculated theoretically.

The discrepancy between theoretical and experimental data is due to the fact that in the calculation one usually neglects long-range intramolecular interaction (p. 93), i.e., interaction between units remote from one another in the chain, but brought close together as a result of coiling of the chain. Attractive or repulsive forces may arise between units of a coiled chain, resulting in a change in volume of the polymer coil. The influence of long-range interaction on the molecular coil volume is known as the *excluded-volume effect*. Making allowance for excluded-volume effect in theoretical calculations means excluding from consideration a number of conformations, mainly strongly coiled ones, since no two units can be situated simultaneously in the same element of volume. If excluded-volume effect is taken into account, the most probable state corresponds to a large-size coil.

The effect of interaction between groups (situated at great distances from one another along the chain) resulting in increase of coil size is equivalent to linear extension of the chain during highly elastic deformation. It may be accepted that the coil is stretched to α times its size found by statistical calculation from the Gauss formula (Chap. 4). Hence, the true coil size is

$$\sqrt{\bar{r}^2} = \alpha\sqrt{\bar{r}_0^2}$$

where $\sqrt{\bar{r}_0^2}$ is the root-mean-square end-to-end distance of the chain found by calculation.

According to Flory, the change in Gibbs free energy with increasing extension, i.e., with increasing α at highly elastic deformation, is given by the equation

$$\frac{\partial \Delta G_{el}}{\partial \alpha} = -3kT\left(\alpha - \frac{1}{\alpha}\right) \qquad (14.60)$$

Apart from the excluded volume, coil size in solutions is affected by interaction between a coil and a solvent. The molecules of the latter penetrate inside the coil, which swells and increases in size.

The change in Gibbs free energy with coil size, caused by swelling, is expressed by the equation

$$\frac{\partial \Delta G}{\partial \alpha} = \frac{6C_M kT\,(k_1 - \psi_1)\,M^{1/2}}{\alpha^4} \qquad (14.61)$$

where k = Boltzmann constant
C_M = parameter depending in a complicated manner on properties of system
M = molecular mass of a polymer.

The total change in Gibbs free energy accompanying the change in coil size equals

$$\frac{\partial \Delta G}{\partial \alpha} = \frac{6C_M kT\,(k_1 - \psi_1)\,M^{1/2}}{\alpha^4} - 3kT\left(\alpha - \frac{1}{\alpha}\right) \qquad (14.62)$$

At equilibrium $\partial \Delta G/\partial \alpha = 0$, and hence,

$$\frac{2C_M\,(k_1 - \psi_1)\,M^{1/2}}{\alpha^4} = \alpha - \frac{1}{\alpha} \qquad (14.63)$$

or

$$\alpha^5 - \alpha^3 = 2C_M \psi_1 \left(1 - \frac{\theta}{T}\right) M^{1/2} \qquad (14.64)$$

It follows from Eq. (14.64) that the size of a real coil increases with increasing molecular mass of a polymer. Even in very dilute solutions the coil size is affected considerably by the entropy of mixing (the ψ_1 term). It also follows from Eq. (14.64) that at a temperature equal to the Flory temperature ($\theta = T$), $\alpha^5 - \alpha^3 = 0$, i.e., $\alpha = 1$. Thus, there is a temperature for each dilute polymer solution, at which it behaves like an ideal solution, the factor α being equal to unity, i.e., long-range intramolecular interaction with the solvent has no effect on the size of the macromolecules, and the coil is in an "unperturbed" state. In an ideal solution chain size depends only on chain flexibility.

All the above reasoning applies only to very dilute solutions, in which the chains do not interact with one another.

14.2.5. Statistical Theory of Swelling of Network Polymers

On the basis of the theory of solutions described above Flory and Rehner derived an equation for the partial entropy of mixing of a low-molecular component penetrating into the phase of a network polymer upon limited swelling of the latter:

$$\Delta S_1 = -R\left[\ln(1 - \varphi_2) + \varphi_2 + \frac{d_2 V_1}{M_c}\left(\varphi_2^{1/3} - \frac{2\varphi_2}{f}\right)\right] \qquad (14.65)$$

By adding the term $\chi_1\varphi_2^2$ to the expression for $T\Delta S_1$ they obtained an equation for the $\Delta\mu_1$ of the low-molecular component:

$$\Delta\mu_1 = RT\left[\ln(1-\varphi_2)+\varphi_2+\chi_1\varphi_2^2+\frac{d_2V_1}{M_c}\left(\varphi_2^{1/3}-\frac{2\varphi_2}{f}\right)\right] \quad (14.66)$$

where φ_2 = volume fraction of a polymer in the swollen sample
d_2 = density of a polymer
V_1 = partial molar volume of a solvent
M_c = molecular mass of a network chain
χ_1 = Huggins constant
f = network functionality. For a tetragonal network $f = 4$.

At equilibrium swelling $\Delta\mu_1 = 0$. Hence,

$$\ln(1-\varphi_2)+\varphi_2+\chi_1\varphi_2^2+\frac{d_2V_1}{M_c}\left(\varphi_2^{1/3}-\frac{2\varphi_2}{f}\right)=0 \quad (14.67)$$

From Eq. (14.67) we can calculate the quantity M_c characterizing the crosslink density of a polymer. To do so we determine experimentally the volume fraction of the polymer in the sample at swelling equilibrium, and parameter χ_1 (p. 429). If the crosslink density in the three-dimensional polymer is not very high, the organic vapour sorption isotherms of three-dimensional and linear polymers of the same chemical structure will coincide. In this case parameter χ_1 is calculated from Eq. (14.34).

In most cases, especially for determining the crosslink density of vulcanized rubbers, a method due to Gee is used. This method is based on the assumption of maximum swelling of the vulcanizate in a liquid whose cohesive energy density equals the c. e. d. of the vulcanizate. After experimentally determining the degree of swelling of the vulcanizate in different liquids, the equilibrium degree of swelling is plotted against the c.e.d. of the liquids. In the ideal case, a single master curve should result for all liquids, having a maximum at the abscissa corresponding to the c.e.d. of polymer $\Delta E_2/V_2$. Parameter χ_1 is then calculated by substituting this quantity into the equation

$$\chi_1 = \frac{BV_1}{RT} = \frac{\left\{\left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2}-\left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right]^2\right\}V_1}{RT} \quad (14.68)$$

It should, however, be pointed out that this method is inaccurate. Even its author noted that the experimental results obtained when using some solvents do not fit on the single master curve. In other words, the degree of swelling of the vulcanizate in different liquids with the same solubility parameter δ is different. This is due to the fact that liquids with different functional groups may have the same δ parameters, but different thermodynamic affinity

for a polymer. The quantity χ_1 is a parameter of energy interaction and cannot serve as a measure of thermodynamic affinity (p. 430).

To obtain more accurate data, correction coefficients are introduced into Eq. (14.68) but satisfactory results are obtained only for elastomeric networks. This raises the fundamental question of the correspondence between experimentally determined and assigned crosslink density. To find the answer to this question, samples with very regularly arranged crosslinks are needed, but their synthesis is rather complicated.

Since models with "regular" networks are unavailable, the theory on which the method is based is imperfect, as will be shown below. For this reason, as has been rightly noted by Flory, estimation of crosslink density of polymers is one of the unsolved problems of modern polymer physics.

Besides, the calculation is based on a network model with crosslinks between macromolecules. However, it has been shown at present that crosslinks may arise between more or less large structural formations. Hence, M_c is not an actually existing chain length, but some equivalent quantity characterizing crosslink density.

14.2.6. Merits and Shortcomings of Present-Day Theory of Polymer Solutions

Flory's and Huggins' theoretical calculations of the thermodynamic functions are of great importance not only for an insight into processes of dissolution of high-molecular compounds, but also for the general theory of solutions. Guggenheim points out that in the theory of solutions "we have advanced a long way since then thanks mainly to the importance attached to solutions of macromolecules".

The existing theory enables calculation of the entropy of mixing of a polymer with a solvent, the value of which is closer to the values found experimentally than to those calculated from Eq. (14.5). This is illustrated vividly by Fig. 14.4. Theory predicts negative deviations from ideality for polymer solutions, and the higher the molecular mass of a polymer, the greater are these deviations. Equation (14.36) for the osmotic pressure of polymer solutions is in some cases in satisfactory agreement with experiment.

The present-day theory of solutions cannot, however, account for a number of new facts, and some of its basic statements are not confirmed by experiment.

1. Theory indicates that only an upper critical solution temperature (UCST) exists for polymer solutions, but it is known

(p. 351) that there is also a lower critical solution temperature (LCST). Hence, there must also be two θ-temperatures.

2. Theory predicts only positive enthalpies of mixing for dissolution of nonpolar polymers in nonpolar solvents; actually (p. 393) exothermal mixing is observed for a number of polymers.

3. According to this theory parameter χ_1 should be a constant quantity independent of concentration; actually, the more polar

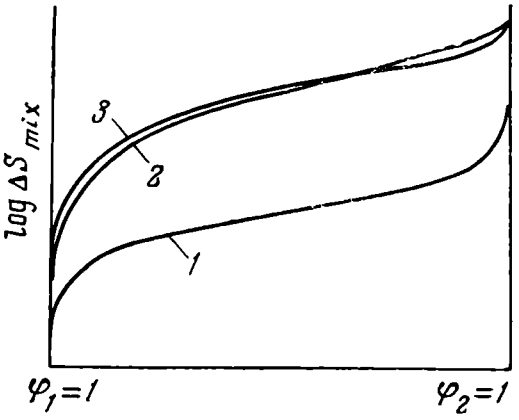

Fig. 14.4. Dependence of entropy of mixing on composition of solution for the system natural rubber-benzene:
1—ideal entropy of mixing; *2*—true entropy of mixing; *3*—entropy of mixing calculated from Eq. (14.23)

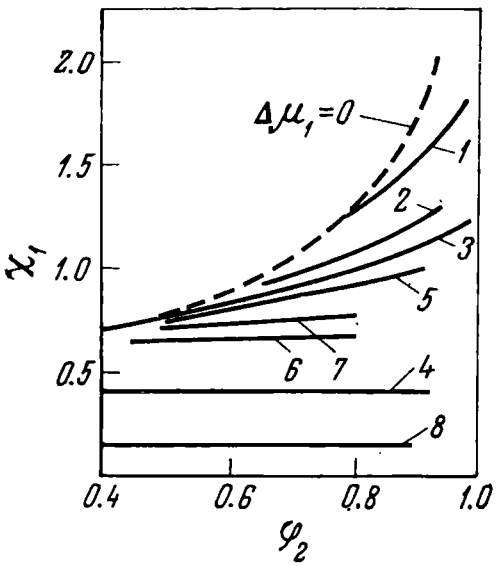

Fig. 14.5. Dependence of parameter χ_1 on volume fraction of polymer in solution:
1—natural rubber-acetone; *2*—natural rubber-methyl ethyl ketone; *3*—natural rubber-ethyl acetate; *4*—natural rubber-benzene; *5*—polystyrene-acetone; *6*—polystyrene-*n*-propyl acetate; *7*—polyisobutylene-benzene; *8*—polyisobutylene-chloroform

the system, the greater is its dependence on the concentration of a solution (Fig. 14.5).

The present-day theory of solutions cannot account for the facts just mentioned; because a number of its conclusions is based on inaccurate assumptions. Some of these are discussed below.

1. The basic theoretical formula for the entropy of mixing is derived on the assumption of athermal mixing, but is used to calculate the entropy of nonathermal mixtures. Though this may be valid, to a certain approximation, for solutions with small heat effects, it is inadmissible for solutions whose formation is accompanied by considerable generation or absorption of heat. The molecules of such solutions display a predominant arrangement (solvation or association), i.e., definite ordering (Chap. 12). According to Guggenheim, molecular orientation plays the main part in such solutions.

For example, in solutions of cellulose nitrate in acetone the solvent molecules arrange themselves in a specific order with respect to the ONO_2 groups, and therefore mixing of acetone with cellulose nitrate should decrease the entropy of acetone. It was shown that, in the case of loosely packed polymers oriented adsorption layers form, and as a result of this the entropy of mixing in concentrated solutions is much less than zero.

The reverse is observed in solutions of polymers with flexible nonpolar chains. Benzene molecules are more strongly oriented in their own medium than in the rubber phase; their penetration into the rubber is accompanied by disorientation, which promotes an additional increase of entropy. That is why the experimental values of ΔS_1 in concentrated rubber solutions are higher than those calculated by the Flory-Huggins equations. In recent years an attempt was made by Tompa and Münster to take into account the effect of mutual orientation of molecules in solutions of both low- and high-molecular substances. The calculations resulted in expressions according to which entropy does not increase on mixing, but decreases.

2. Though derived on the basis of the concept of flexible chains, Flory's and Huggins' equations are often applied to solutions of polymers of any flexibility. Obviously, with decreasing chain flexibility the difference between the value of ΔS_1 calculated from equations (14.23)-(14.25) and the experimental value of $\Delta S_{1\,exp}$ increases. The theoretical equations do not apply to very dilute solutions of even elastic flexible polymers because their chains are coiled, which is not taken into account by the calculation.

3. It can be shown that the quantity φ_2, which Flory calls the volume fraction of a polymer [Eq. (14.22)] is really the "fraction of sites" and coincides with volume fraction only under the condition that

$$\frac{M_0}{M_1} = \frac{d_2}{d_1} \tag{14.69}$$

where M_1 and M_0 = molecular masses of a solvent and a polymer chain unit

d_1 and d_2 = densities of a solvent and a polymer.

Relation (14.69) is not always satisfied by far.

This theory, like other theories of solutions, is based on the rough quasicrystalline model, which, as was rightly pointed out by Flory and coworkers, artificially depresses the basic property of liquids, namely, the irregularity in mutual arrangement of their molecules.

The most serious defect of the lattice theory of solutions is that the effect of change in volume of a solution is neglected. Constancy of volume on mixing of components is a direct consequence

of this theory since one of its essential assumptions is absence of change in the movement of the component molecules relative to the position of equilibrium in each lattice cell. It follows hence that entropy can increase only as a result of an exchange of sites by unlike molecules. Thus, the Flory-Huggins theory takes into account only the combinatorial entropy of mixing (p. 398). The only theory that makes allowance for the volume change effect is that of Prigogine.

14.3. PRIGOGINE'S THEORY

One of the basic propositions of this theory is the assumption that the free volumes of a polymer and a solvent are different, this being very close to the idea developed in the work of V. Kargin's school that the packing of polymer molecules differs from that of their hydrogenated monomers.

The most substantial difference between amorphous linear polymers and low-molecular liquids is that in the former the units are connected by covalent bonds of a length smaller than that of the intermolecular bonds in the liquid. For this reason polymerization always involves contractions, i.e., the free volume of a polymer is always smaller than the volume of its low-molecular analogue (p. 400).

The change in free volume of a polymer on mixing has the opposite sign to the change in free volume of a solvent, namely: the free volume of a solvent decreases, as it were, whereas the free volume of a polymer increases. These two effects do not compensate each other, however, because $\Delta V^{M} \neq 0$, and usually the total volume decreases (p. 400).

The differences in free volumes of a polymer and a solvent are responsible for the differences in their thermal expansion coefficients; the expansion coefficient of a polymer is much smaller than that of a solvent. For this reason at room, and especially at elevated temperatures, a monomeric liquid should expand much more than a polymeric one. However, the solvent is in a compact state, as it were, being similar in this respect to a condensed compressed gas. The heat expended on this "compression" should be equal to the "heat of vaporization" and have the opposite sign. This negative contribution, which is a result, as it were, of interaction of the solvent molecules with one another, adds to the positive enthalpy of mixing — the result of dispersional interaction between the nonpolar polymer and the solvent.

The net result is that in such systems the total heat of mixing may become negative ($H^{E} < 0$), which is observed, for instance, when polyisobutylene is dissolved in lower normal alkanes (p. 394). Mixing of very polar substances with dipole-dipole interaction or

intermolecular hydrogen bonds is also accompanied by generation of heat and a decrease of entropy. Thus, in both cases $H^E < 0$ and $S^E < 0$, which is a necessary condition for the presence of an LCST (p. 407).

These qualitative ideas are supported by quantitative calculations.

In the first version of the theory its authors used the lattice or cellular solution model, but in contrast to other theories, the rigid lattice, incapable of volume changes, was replaced by a lattice consisting of cells whose volume could vary depending on pressure, temperature, and the composition of solution.

In later papers Prigogine and his coworkers make no assumptions as to the existence of lattices in solutions, and show the possibility of applying the *law of corresponding states* (see below) to liquids with chain molecules; certain assumptions are made as to the structure of such liquids.

14.3.1. Pure Liquids with Chain Molecules

A chain molecule is regarded as a sequence of quasispherical rigid segments which may differ in chemical composition or structure. Two types of interaction forces are characteristic of such a liquid: valency and intermolecular forces (p. 93), differing sharply in energy and range. The properties of liquids that depend only on valency forces, i.e., are determined by internal degrees of freedom, are called *internal* properties. The properties of liquids that depend on intermolecular forces, i.e., are determind by external degrees of freedom, are called *external* properties. Internal degrees of freedom are the movements of nuclei and electrons, as well as valency and deformational vibrations of chemical bonds. By external degrees of freedom are meant the translational and rotational movement of the molecule as a whole, and its internal rotation. Hindered internal rotation may be imagined as superposition of torsional vibrations on the sequence of transitions between different states of rotational isomers. The former movement may be classed as an internal motion, but the latter is an external motion affected by the packing density of the molecules, and hence by the volume of the liquid. The internal properties of liquids depend on temperature; the external properties, on temperature and volume.

Prigogine's theory takes into account only external properties, and hence a liquid with chain molecules is regarded as a cluster of quasifree segments interacting with one another only through van der Waals forces. There is, however, a difference between such a cluster and a cluster of free spherical molecules. The existence

of chemical bonds between the segments affects their behaviour as follows:

1. The surface around the segment is only partly available for intermolecular interactions, the rest of it being blocked by the neighbouring segments of the same molecule.

Suppose a chain consisting of n atoms can be regarded as a sequence of r quasispherical segments. The number of external contacts q of these r segments is much smaller than the number of external contacts of independent spherical segments; q and r are close in value.

2. Each segment of this chain has less than three degrees of freedom an independent spherical molecule would have. If the number of external degrees of freedom of a chain molecule is $3c$, then c is the number of equivalent spherical molecules.

It is assumed that all external contacts between segments are characterized by a potential of the same type, e.g., the Lennard-Jones potential:

$$\varphi(R) = 4\varepsilon^*\left[\left(\frac{\sigma^*}{R}\right)^{12} - \left(\frac{\sigma^*}{R}\right)^{6}\right] \tag{14.70}$$

where ε^* = energy of contact at 0 K
σ^* = distance over which this contact is accomplished (diameter of sphere of action)
R = distance between molecules
$\varphi(R)$ = energy of intermolecular interaction.

Thus, a liquid with chain molecules can be characterized by two parameters ε^* and σ^* of each segment and three dimensionless parameters q, r, and c, which have the sense of the effective number of segments.

The cohesive energy per molecule of a monomeric liquid is proportional to $Z\varepsilon^*$, and of a polymeric liquid, to $qZ\varepsilon^*$, where Z is the coordination number of the liquid and $q\varepsilon^*$ is the energy of external contacts of n segments.

If there are N chain molecules, the cohesive energy of the liquid is $NqZ\varepsilon^*$; its volume is $Nr\sigma^*$, and its entropy Nck, k being Boltzmann's constant.

The quantities

$$U_0 = q\varepsilon^*, \quad v_0 = r\sigma^*, \quad \text{and} \quad s_0 = ck \tag{14.71}$$

are called molecular units.

14.3.2. Law or Principle of Corresponding States

The law of corresponding states, formulated originally for real gases, asserts that at corresponding temperatures and pressures the corresponding volumes of substances should be the same.

The *corresponding state of* two substances is a state at which they have equal reduced pressures, temperatures, and volumes. *Reduced variables* are dimensionless variables, usually obtained by dividing the temperature, volume, and pressure of a gas by the corresponding critical parameters; the reduced temperature $\tau = T/T_{cr}$; the reduced pressure $\pi = p/p_{cr}$, and the reduced volume $\omega = V/V_{cr}$.

Pitzer and later Guggenheim showed that the law of corresponding states could be applied successfully to liquids with spherical molecules, for which a universal equation of state $p^*(V^*T^*)$ could be found if the pressure, volume, and temperature were expressed as reduced variables (denoted by *).

The possibility of applying the law of corresponding states to liquids with chain molecules was first demonstrated by Prigogine and his collaborators. Any molar thermodynamic function of these substances can be obtained in the reduced form. The configurational energy, volume, configurational entropy, etc., of a polymeric liquid are functions of temperature and the number of atoms n in the chain [$V(T, n)$; $U(T, n)$; $S(T, n)$, etc.]. Reduced variables should be independent of the nature of the substance and should be a function of temperature alone. To achieve this the normalizing or reduction parameter (v_0, u_0, s_0, etc.) must be a function only of the nature of the substance, i.e., in the case of a homologous series of substances it should be dependent on n only.

Reduction of thermodynamic variables can be accomplished in different ways. One method is to plot the experimental data for volume vs. temperature for various liquids on a logarithmic graph and then shift the resulting curves in the x and y directions until they coincide with the V vs. T curve of a liquid chosen as the standard. In such a case the amount of shift does not give the absolute value of the reduction parameter, but the ratio $v_0/v_{0,\,st}$ and $T_0/T_{0,\,st}$. In this way it was shown that a master V^* vs. T^* curve can be obtained for all n-alkanes.

Simha and Havlik showed that all experimental data on the volume versus temperature dependence for homologous series of alkanes (from methane to polyethylene), polystyrene (from the dimer to a polymer of infinite molecular mass), poly(ethylene oxides), polydimethylsiloxanes, and fluorinated alkanes of different degrees of polymerization fit on a single master curve. All these studies confirm the applicability of the law of corresponding states to polymeric liquids. Simha and his coworkers demonstrated that the volume versus temperature dependence of polymeric glasses also obeys the law of corresponding states.

In Prigogine's theory the reduction parameters are given by Eq. (14.71). The reduced variables are expressed by the following

equations:

Reduced energy $$U^* = \frac{U}{Nu_0} = \frac{U}{Nq\varepsilon^*} \qquad (14.72a)$$

Reduced volume $$V^* = \frac{V}{Nv_0} = \frac{V}{Nr\sigma^{*3}} \qquad (14.72b)$$

Reduced entropy $$S^* = \frac{S}{Ns_0} = \frac{S}{Nck} \qquad (14.72c)$$

Reduced pressure $$p^* = -\left(\frac{\partial U^*}{\partial V^*}\right)_{S^*} = \frac{pv_0}{u_0} \qquad (14.72d)$$

Reduced temperature $$T^* = \left(\frac{\partial U^*}{\partial S^*}\right)_{V^*} = \frac{Ts_0}{u_0} \qquad (14.72e)$$

Reduced heat capacity $$c_p^*(T^*) = \frac{c_p(T, n)}{Ns_0} \qquad (14.72f)$$

The reduced temperature is basically the ratio of the kinetic energy of the substance, depending on the number of degrees of freedom, to its cohesive energy, i.e., it depends on the so-called structural factor c/q:

$$T^* = \frac{T}{T_0} = \frac{3ckT}{qZ\varepsilon^*} \approx \frac{c}{q} \cdot \frac{kT}{Z\varepsilon^*} \qquad (14.73)$$

14.3.3. Thermodynamics of Mixtures of Liquids with Chain Molecules

Prigogine's theory predicts that the molar configurational (p. 398) thermodynamic variables of a mixture of liquids with chain molecules will also obey the law of corresponding states.

The simplest case is that of a molecular mixture of components whose molecules are members of the same homologous series, i.e., differ only in size, but have the same ε^* and σ^* values. An example is a mixture of an amorphous liquid polymer with its low-molecular analogue or with its hydrogenated monomer. The normalizing parameters of such systems are additive values of the corresponding normalizing parameters of the pure components, i.e.,

$$\langle v_0 \rangle = N_1 v_{0,1} + N_2 v_{0,2} \qquad (14.74)$$

$$\langle u_0 \rangle = N_1 u_{0,1} + N_2 u_{0,2}, \text{ etc.} \qquad (14.75)$$

where N_1 and N_2 are the mole fractions of the components.

Similarly:

$$\langle q \rangle = N_1 q_1 + N_2 q_2 \qquad (14.76)$$

$$\langle c \rangle = N_1 c_1 + N_2 c_2 \qquad (14.77)$$

Hence, according to Eq. (14.73) the reduced temperature of the mixture

$$\langle T^* \rangle = \frac{T}{\langle T_0 \rangle} = \left\langle \frac{c}{q} \right\rangle \frac{kT}{\varepsilon^*} = \frac{(N c_1 + N c_2) kT}{(N_1 q_1 + N_2 q_2) \varepsilon^*} =$$

$$= \frac{N_1 c_1}{N_1 q_1 + N_2 q_2} \cdot \frac{kT}{\varepsilon^*} + \frac{N_2 c_2}{N_1 q_1 + N_2 q_2} \cdot \frac{kT}{\varepsilon^*} \qquad (14.78)$$

Multiplying and dividing each term by q_1 and q_2, we get

$$\langle T^* \rangle = X_1 T_1^* + Z_2 T_2^* \qquad (14.79)$$

The expression

$$X_1 = \frac{N_1 q_1}{N_1 q_1 + N_2 q_2} \qquad (14.80)$$

is the *surface fraction*, i.e., the ratio of the number of external contacts of the molecules of component 1 to the total number of external contacts in the solution. This fraction should be very close to the fraction of all segments of species 1. In other words, it may be expected that if $q \approx r$, $X_1 = \varphi_1$. Hence, the reduced temperature of the mixture

$$\langle T^* \rangle = \varphi_1 T_1^* + \varphi_2 T_2^* \qquad (14.81)$$

where T_1^* and T_2^* = reduced temperatures of pure components
φ_1 and φ_2 = their volume fractions in the solution.

On the basis of what has been said above, the volume, energy, entropy of mixing, and the corresponding excess thermodynamic functions can be calculated. For example, the excess volume of mixing $\Delta V^M = V_{sol} - N_1 V_1 - N_2 V_2$.

Substituting the reduced variables, we obtain

$$\Delta V^M = \langle v_0 \rangle V^* \{ \langle \langle T^* \rangle \rangle - [N_1 v_{0,1} V^* (T_1^*) + N_2 v_{0,2} V^* (T_2^*)] \} \qquad (14.82)$$

Assuming that

$$\frac{N_1 v_{0,1}}{\langle v_0 \rangle} = \frac{N_1 v_{0,1}}{N_1 v_{0,1} + N_2 v_{0,2}} \quad \text{and} \quad \frac{N_2 v_{0,2}}{\langle v_0 \rangle} = \frac{N_2 v_{0,2}}{N_1 v_{0,1} + N_2 v_{0,2}}$$

are equal to the volume fractions φ_1 and φ_2, we get

$$\Delta V^M = \langle v_0 \rangle \{ V^* (\langle T^* \rangle) - [\varphi_1 V^* (T_1^*) + \varphi_2 V^* (T_2^*)] \} \qquad (14.83)$$

Figure 14.6 presents the reduced volume versus temperature curve for a homologous series of substances and shows the reduced volumes T_1^* and T_2^* for the low-molecular homologue (solvent) and the high-molecular homologue. Point B represents the reduced volume of the mixture, and point A is the simple sum of reduced volumes of the components. It is evident from the figure

that the difference ΔV^M should be negative in accordance with the reasoning on p. 442, and with an experiment.

The energy of mixing can be calculated by analogy with ΔV^M:

$$\Delta U^M = U_{sol} - N_1U_1 - N_2U_2 =$$
$$= \langle u_0 \rangle \{U^*(\langle T^* \rangle) - [\varphi_1 U_1^*(T_1^*) + \varphi_2 U_2^*(T_2^*)]\} \qquad (14.84)$$

Different models of the liquid state and experimental data for *n*-alkanes show that the curve for U^* vs. T^* is also concave to the ordinate axis, at least at elevated temperatures, and hence, ΔU^M is also negative.

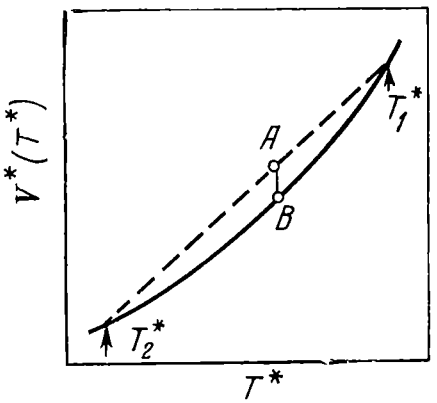

Fig. 14.6. Reduced volume versus reduced temperature for liquid polymer homologues

Thus, Prigogine's theory predicts that when polymers dissolve, even if there is no difference in chemical constitution of the components (polymer-hydrogenated monomer), the values of ΔV^M and ΔU^M are different from zero. This is due only to the difference in chain lengths and thermal expansion coefficients of the components.

The contribution to the thermodynamic functions of mixing due only to difference in size of the component molecules is called the *structure effect* in the Prigogine theory; this effect depends on the structural factor c/q.

Negative values of ΔV^M cause a negative contribution to the entropy of mixing ΔS^M, which in the case of liquid amorphous polymers dissolved in their low-molecular analogues is more substantial than the negative value of ΔU^M. For this reason the noncombinatorial contribution of the free energy of mixing is positive ($G^E > 0$), which is the reason for phase separation at high temperatures.

Prigogine's theory was developed further in the work of Patterson who derived an equation for the temperature dependence:

$$\chi = G\left[-\frac{U^*(T^*)}{T}v^2 + \frac{c_p^*(T^*)}{2}\tau^2\right] \qquad (14.85)$$

where G = number of external degrees of freedom of solvent molecules
U^* = reduced configurational internal energy
c_p^* = reduced configurational heat capacity of a solvent
T = reduced temperature
v and τ = molecular temperature-independent parameters, τ decreasing with chain length of a solvent.

The first term in Eq. (14.85) is determined by the energy of formation of contact between polymer segments and a solvent, and by the difference in size of the segments, and is a positive decreasing function of temperature. The second term corresponds to the "structural" contribution arising due to the change in free volume when a more closely packed polymeric liquid is mixed with a less closely packed solvent. This term is a positive and increasing function of temperature. Hence, parameter χ decreases with increasing temperature, passes through a minimum and then increases again. Thus, Eq. (14.85) predicts an extremal nature of the variation of the solubility parameter with temperature, which is confirmed by experiment, and thus, also predicts the existence of UCST and LCST for the system polymer-solvent.

Delmas and Patterson showed that the second Virial coefficient A_2 of the system polyisobutylene-*n*-pentane and the size of its molecular coils decrease on approaching the LCST, as well as on approaching the UCST, and that the macromolecules acquire the same unperturbed sizes; hence, there is a second θ-temperature, which they suggest calling the Rowlinson temperature.

The Prigogine-Patterson theory makes it possible to predict the dependence of LCST on the length of solvent molecules and the effect of pressure on the position of the LCST, which is much weaker than on the UCST. This theory predicts a concentration dependence of partial enthalpies of mixing, which is confirmed by an experiment.

However, the theory in the form suggested by its authors is very complicated, mainly owing to the difficulty of determining the reduction parameters.

14.4. FLORY'S NEW THEORY

A considerable step forward is the new theory of Flory and coworkers, based on all the physical presumptions of the Prigogine theory, but making it possible to calculate comparatively simply all the reduction parameters and the reduced variables, since they are connected by strict thermodynamic relations with such constants of substances as coefficients of thermal expansion α_p, isothermal compressibility β_T and thermal pressure γ, which are tabulated.

Flory, Vrij, *et al.* rightly point out that treatment of liquids "... by methods which join rigor with tractability of result is an objective for which there is yet small hope of fulfilment" and for this reason they "sacrifice rigor in favour of simplicity".

Without going into the details of Flory's new theory we shall dwell on the basic ideas of his calculation.

Suppose we have N chains, each consisting of r segments. If the volume of liquid is V, the volume of a segment can easily be

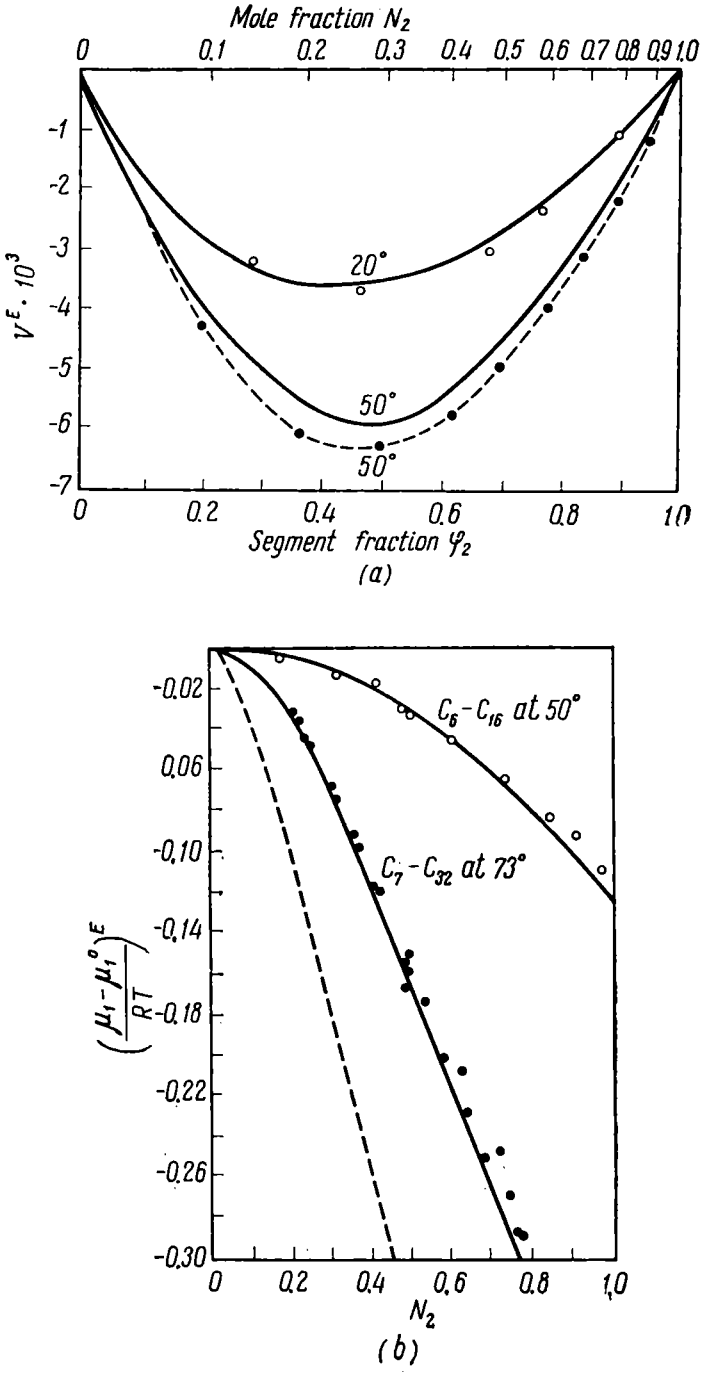

Fig. 14.7. (*a*) Reduced excess volumes for C_6—C_{16} mixtures against the segment fraction φ_2 of the latter component. Solid curves have been calculated from the reduced equation of state. The dashed line has been drawn through experimental points. (*b*) Excess chemical potentials for the system C_6—C_{16} at 50 °C and for C_7—C_{32} at 73 °C plotted against the mole fraction N_2 of the high-molecular component. Solid lines have been calculated from the equation of the principle of corresponding states. The dashed line represents the lattice contribution for the latter system

calculated from the equation

$$V = \frac{V}{rN} \tag{14.86}$$

The reduction parameter is what is known as the net volume of a segment v, i.e., the volume of a segment under the assumption that all its hard spheres are in contact. The difference between these two segment volumes reflects the free volume per segment.

The reduced volume V^* is calculated from the equation

$$V^* = \frac{v}{v^*} \tag{14.87}$$

The main equation of the theory, which is derived rigorously, is the equation

$$(V^{*1/3} - 1) = \frac{\alpha_p T}{3}(1 + \alpha T) \tag{14.88}$$

which makes it possible, with the thermal expansion coefficient of the liquid known, to calculate the reduced volume V^* very simply, and then the reduction parameter v^* from Eq. (14.87).

Using another rigorous thermodynamic equation

$$\frac{V^{*1/3} - 1}{V^{*4/3}} = T^* \tag{14.89}$$

the reduced temperature T^* can be calculated. The reduction parameter for pressure is calculated by the equation

$$p^* = \frac{\alpha_p T V^{*2}}{\beta_T} \tag{14.90}$$

for which α_p and β_T of the liguid must be known.

In this way all the reduction parameters and all the normalizing factors are calculated consecutively.

Knowing the reduced values for the components, the reduced values for their mixtures are calculated by Eqs. (14.74), (14.75), (14.76), etc.

The resulting values of thermodynamic parameters are in satisfactory agreement with experiment, as it follows from Figs. 14.7*a* and *b*.

Figure 14.7*a* is the concentration dependence of the excess volumes of mixing for alkane mixtures at different temperatures. It is evident that at 50 °C theory and experiment are in excellent agreement, but a slight discrepancy is observed at 20 °C.

Figure 14.7*b* shows the concentration dependence of $\Delta\mu/RT$ values calculated according to Flory's new and old theories. It follows from the figure that the theory based on the network model of solution is not confirmed by an experiment, but the new theory describes it satisfactorily.

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CHAPTER 15

Mechanical Properties of Polymer Solutions and Gels

15.1. RHEOLOGICAL PROPERTIES OF SOLUTIONS AND GELS OF POLYMERS

When a solvent is added to a polymer, its glass-transition and flow temperatures decrease. Depending on the quantity of the solvent added, i.e., on the concentration of a solution, it may be in a glassy, rubber-like or viscofluid state. Irrecoverable flow deformation is of fundamental importance to the fluid solution, just as to the melt (Chap. 10); however, rubber-like deformation interferes with it, and this deformation is especially important to gels. Hence, solutions and gels of polymers generally possess viscoelastic properties, whose main parameters are the viscosity coefficient and the shear modulus.

The viscosity of a polymer solution, just as of a melt, can be a function of stress and shear rate; it always depends on the molecular mass of a polymer and temperature. However, the viscosity of a solution also depends on its concentration and the nature of a solvent, on its thermodynamic affinity for a polymer.

It is easiest to assume that the coefficient of viscosity of a solution is the simple sum of the viscosity coefficient of its components, i.e.,

$$\eta = \eta_1\chi_1 + \eta_2\chi_2 \tag{15.1}$$

where η, η_1, and η_2 = coefficients of viscosity of solution and components

χ_1, and χ_2 = mole fractions of components in the solution.

However, experiment shows that in ideal solutions relation (15.1) does not apply. The dependence of the viscosity of a solution of two low-molecular liquids on composition is usually a curve rather than a straight line. In some systems with certain component ratios, the viscosity of the solution may be higher than

that of the more viscous component or lower than that of the less viscous component.

Dissolving a polymer involves mixing of two components with sharply different viscosity coefficients. For example, the viscosity of a polymer may be 10^{11} to 10^{14} poises (Chap. 10) whereas the viscosity of the low-molecular component is about 0.01 poise. Therefore, when a polymer is added to a solvent, the viscosity of a system increases, when a low-molecular liquid is added to a polymer, it decreases, and when the concentration changes, the viscosity of a solution changes by 13-15 decimals. Since polymer flow is connected with the jumps of the chain segments, free volume is of great importance. Therefore, it is expedient to express the concentration of a solution in volume fractions of components, and this is usually done for solutions of a high concentration. For dilute solutions, concentration is expressed in g/100 ml or in g/ml.

The flow mechanism of dilute polymer solutions differs from that of concentrated ones, and therefore they will be considered separately.

15.2. DILUTE POLYMER SOLUTIONS

15.2.1. Absolute, Relative, Reduced, and Intrinsic Viscosity

The term *dilute* is usually applied to polymer solutions containing not more than 1 g of a polymer per 100 ml of a solution. At such concentrations of low-molecular substances the solute molecules in solutions practically do not interact with one another. In polymer solutions, owing to the very large size of macromolecules higher dilutions are required for complete separation. As has been mentioned above, polymer molecules interact in solutions containing as little as 0.5 g and even less per 100 ml, forming associates. Therefore, in studying properties due to the presence of isolated macromolecules, data should always be extrapolated to infinite dilution.

It is quite obvious that the addition of a highly viscous polymer to a solvent of low viscosity will raise the viscosity of the solution. The addition of insignificant amounts of polymer causes a sharp increase of viscosity. The viscosity of even a very dilute solution of a polymer of high molecular mass may be 10 or 20 times higher than that of the solvent.

The viscosity coefficient of such solutions is determined in capillary viscometers. The volume of the sphere V containing the solution, the capillary length L and the capillary radius R must be measured accurately. The viscosity coefficient η of a liquid or

solution is calculated from the Poiseuille equation:

$$\eta = \frac{\pi \Delta p R^4}{8LV} \tau \tag{15.2}$$

where Δp = difference of pressures at capillary ends
τ = time of efflux determined by experiment.

If the liquid flows out of the capillary by gravity, then

$$\Delta p = gHd \tag{15.3}$$

where g = gravity acceleration
H = difference of liquid levels in arms of instrument
d = relative density of liquid.

Substituting the value of Δp from Eq. (15.3) into Eq. (15.2), we obtain

$$\eta = \frac{\pi g H d R^4}{8LV} \tau \tag{15.4}$$

As the liquid flows out of the capillary the weight of its column changes, i.e., the quantity H is variable. For this reason, to obtain precise results specially designed viscometers are used, in which the liquid level in the capillaries is kept constant. Substitution of all the values in Eq. (15.4) gives the *absolute coefficient of viscosity* of the liquid or solution.

If the measurements are always carried out in the same viscometer, the values of V, L, and R remain constant; then the liquid column height should also be constant, and hence

$$\eta = Kd\tau \tag{15.5}$$

The quantity

$$K = \frac{\pi H R^4 g}{8LV} \tag{15.6}$$

is called the *viscometer constant* and is calculated from the time of efflux of a liquid of known viscosity from the viscometer in question:

$$K = \frac{\eta_0}{d_0 \tau_0} \tag{15.7}$$

where η_0, d_0, and τ_0 are the viscosity coefficient, density, and time of efflux of the calibration liquid, respectively.

In studying dilute polymer solutions, instead of the absolute value of the viscosity coefficient one often uses the so-called *relative viscosity* (*viscosity ratio*), which is the ratio of solution viscosity to pure solvent viscosity:

$$\eta_r = \frac{\eta_{sol}}{\eta_{solv}} \tag{15.8}$$

To determine the relative viscosity, the times of efflux of the solution and the solvent are measured in the same viscometer,

taking the density of the dilute solution equal to that of the pure solvent ($d = d_0$). Then

$$\eta_r = \frac{\tau}{\tau_0} \tag{15.9}$$

The efflux times of the solution τ and the solvent τ_0 are determined at a strictly fixed temperature, because viscosity depends on temperature (Chap. 10). It should be borne in mind that Poiseuille's law is valid only for laminary flow, which can be maintained by observing a definite relation between the viscosity of the liquid, the capillary radius, and the rate of efflux. It is recommended to select viscometers with such capillaries that the efflux time of the pure solvent should be not less than 80-120 s.

When determining viscosity it should be taken into account that in polymer solutions equilibrium is reached very slowly. Solutions may be prepared and stored at temperatures different from those at which the viscosity is measured. A variation of temperature changes the structure of the solution, and therefore also its viscosity, which results in different efflux times. To obtain accurate viscosity values the solutions should be held at the given temperature in a thermostat for a certain definite time required to establish equilibrium in the solution. True viscosity values are ones which do not change in time.

The *specific viscosity* of a solution is the viscosity increase (due to the presence of a polymer) divided by the viscosity of the pure solvent:

$$\eta_{sp} = \frac{\eta_{sol} - \eta_{solv}}{\eta_{solv}} = \eta_r - 1 \tag{15.10}$$

The *reduced viscosity* is the ratio of the specific viscosity to the concentration:

$$\eta_{red} = \frac{\eta_{sp}}{c} \tag{15.11}$$

The relative, specific, and reduced viscosities of even dilute solutions increase with increasing concentration.

The variation of reduced viscosity with concentration in dilute solutions ($c < 1$ g/100 ml) is given by a straight line (Fig. 15.1), described by the equation

$$\frac{\eta_{sp}}{c} = a_1 + a_2 c \tag{15.12}$$

where a_1 = intercept on ordinate
a_2 = slope of the line.

Obviously,

$$a_1 = \left(\lim \frac{\eta_{sp}}{c}\right)_{c \to 0}$$

This quantity, which is independent of the concentration of a solution and is the limiting value of the reduced viscosity, is known as the *limiting viscosity number* or *intrinsic viscosity* of the solution [η]:

$$[\eta] = \left(\lim \frac{\eta_{sp}}{c}\right)_{c \to 0} \tag{15.13}$$

Since specific viscosity, like relative viscosity, is a dimensionless quantity, according to Eq. (15.13) the intrinsic viscosity has the dimension of the reciprocal of the concentration, i.e., ml/g or dl/g.

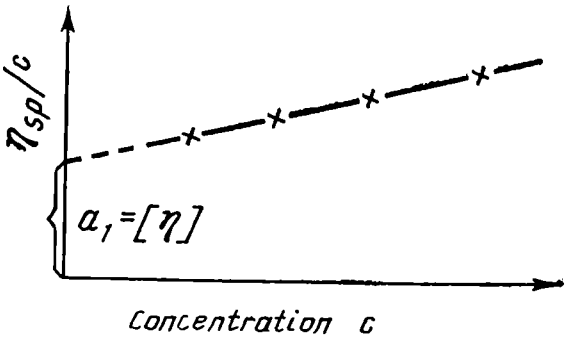

Fig. 15.1. Dependence of reduced viscosity of a dilute polymer solution on concentration

Substituting expression (15.13) into Eq. (15.12), we get

$$\frac{\eta_{sp}}{c} = [\eta] + a_2 c \tag{15.14}$$

15.2.2. Newtonian and Non-Newtonian Flow

The viscosity of even dilute polymer solutions may be dependent on an applied shear stress or shear rate. Hence, dilute polymer solutions may behave like non-Newtonian liquids.

Under the action of an applied stress the long macromolecules straighten out and orient themselves in the flow. However, their orientation is disturbed by thermal motion. The degree of orientation therefore depends on the ratio between the intensity of thermal motion and the magnitude of the shear stress or rate applied. The larger the shear rate, the smaller will be the effect of thermal motion, the greater the effect of orientation, and the lower the viscosity. At constant temperature the more diluted the solution, the higher will be the intensity of thermal motion. For this reason the effect of viscosity lowering with increasing shear stress is more pronounced in more concentrated solutions, where the degree of orientation is higher (Table 15.1). With increasing shear rate the viscosity coefficient decreases to a definite value corresponding to extreme orientation of the chains.

TABLE 15.1. *Relative Viscosity of Solutions of Natural Rubber in Benzene*

Pressure, g/cm²	Relative viscosity at concentration						
	0.05%	0.1%	0.2%	0.4%	0.6%	0.8%	1.0%
10.5	1.18	1.46	2.48	5.42	7.14	11.31	17.71
20.5	1.18	1.57	2.27	4.57	6.55	9.80	15.41
40.5	1.17	1.41	2.08	4.48	6.22	9.68	14.03
60.5	1.18	1.37	2.07	4.24	5.61	7.61	13.47

Thus, in the case of dilute polymer solutions the dependence of the logarithm of viscosity on shear stress is represented by a complete flow curve (Fig. 15.2), the initial portion of which corresponds to the initial Newtonian viscosity, and the final portion, to

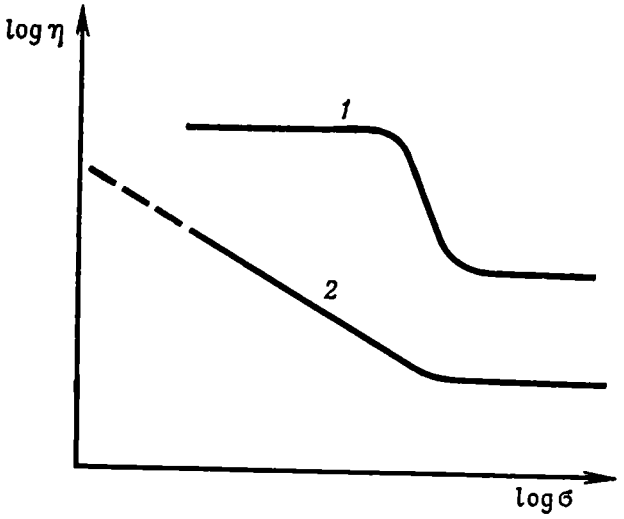

Fig. 15.2. Viscosity vs. shear stress for a dilute solution

the minimum Newtonian viscosity at extreme orientation of the macromolecules. The middle portion of the curve corresponds to the structural viscosity (Chap. 9). In determining the intrinsic viscosity, measurements should be made at Newtonian flow conditions. This is achieved by carrying out experiments at very low shear stresses and rates or by extrapolating the $\log \eta$ vs. $\dot{\gamma}$ or $\log \eta$ vs. σ_{sh} dependencies obtained to zero rate or zero stress.

15.2.3. Mechanism of Flow of Dilute Polymer Solutions

The nature of the high viscosity of dilute polymer solutions was for a long time interpreted incorrectly. It was thought that the high viscosity of the solutions was due to thick solvate layers, which were supposed to form around the micelles.

It has now been established that polymer solutions contain no micelles or polysolvate layers (Chap. 12). The previous ideas as to the reasons for the high viscosity of polymer solutions have proved untenable.

The present-day interpretation of the nature of viscosity of dilute polymer solutions is based on analysis of their hydrodynamic properties, i.e., properties related to the movement of macromolecules in a solution. Translational movement of macromolecules relative to solvent molecules may be random (Brownian motion), directed (diffusion), or movement in a centrifugal field (sedimentation). In a laminary flow at a definite shear rate different parts of the macromolecule move at different rates, depending on whether they are in the zone of rapid flow or in that of comparatively slow flow. As a result, the macromolecule is under the action of a couple of forces which makes it rotate in the flow.

Rotation and translational movement of macromolecules causes friction between their segments and the solvent molecules, the macroscopic manifestation of which is an increase in viscosity of the solution compared to the viscosity of the pure solvent. The increase in viscosity due to rotation of individual macromolecules is estimated by the intrinsic viscosity $[\eta]$, i.e., by the reduced viscosity extrapolated to zero concentration.

In a dilute solution the long flexible macromolecule curls up into a coil. There are two opposite points of view on the behaviour of such a coil during flow.

According to the first point of view the coil is regarded as a formation through which the solvent molecules can pass freely. This means that the movement of the medium is independent of the movement of segments or that each segment experiences the same friction in the surrounding medium as in the absence of other segments.

The second viewpoint is essentially that the macromolecule in coil form retains a definite amount of solvent enclosed by it and moves together with this solvent. Such a coil is a spherical particle of effective radius R_{eff} (radius of swollen coil sphere), impermeable to the rest of the solvent *.

Einstein derived the following equation for spherical particles which do not interact with the solvent:

$$\eta_{sp} = 2.5\varphi \qquad (15.15)$$

where φ is the volume fraction of spherical particles.

It may be assumed that under the action of a shear stress the coil with the solvent enclosed by it behaves like an Einsteinian

* These two models of extreme cases are referred to as the *free-draining coil* and the *impermeable coil.* — *Tr.*

sphere, and hence, the specific viscosity of solution should obey Eq. (15.15):

$$\eta_{sp} = 2.5\varphi = 2.5\frac{v}{V} = 2.5\frac{n\frac{4}{3}\pi R_{eff}^3}{V} \qquad (15.16)$$

where v = volume of spherical particles
V = volume of solution
R_{eff} = effective radius of sphere
n = number of spherical particles.

Dividing the number of spherical particles by Avogadro's number N_A gives the number of moles of a polymer.

Thus,

$$\frac{n}{N_A} = \frac{g_2}{M} \quad \text{or} \quad n = \frac{g_2 N_A}{M}$$

Hence,

$$\eta_{sp} = 2.5\frac{g_2 N_A}{MV} \cdot \frac{4}{3}\pi R_{eff}^3 \qquad (15.17)$$

where M is the molecular mass of a polymer.

The ratio $g_2/V = c$ is the concentration of a polymer in solution in g/ml. Therefore

$$\frac{\eta_{sp}}{c} = 2.5\frac{N_A}{M} \cdot \frac{4}{3}\pi R_{eff}^3 \qquad (15.18)$$

Extrapolation to zero concentration gives

$$[\eta] = \left(\lim \frac{\eta_{sp}}{c}\right)_{c\to 0} \approx \frac{R_{eff}^3}{M} \qquad (15.19)$$

If the effective coil radius is taken as proportional to $\sqrt{M}$, then

$$[\eta] \propto \frac{(\sqrt{M})^3}{M} = \sqrt{M} \qquad (15.20)$$

Thus, theoretically the intrinsic viscosity of the impermeable coil surrounded by a solvent is proportional to $\sqrt{M}$, whereas for the free-draining coil through which the solvent molecules pass freely it is proportional to M.

Experiment shows that the quantity $[\eta]$ is related to molecular mass by the equation

$$[\eta] = KM^a \qquad (15.21)$$

where a lies in most cases between 0.6 and 0.8.

Equation (15.21) has become known as the Mark-Kuhn-Houwink equation and is widely used for determining molecular masses of polymers (Chap. 16).

The discrepancy between theory and experiment is due to the excluded-volume effect (p. 436), i.e., to the fact that a real coil is α times larger than an ideal one. Hence,

$$[\eta] = K\alpha^3 M^{1/2} \tag{15.22}$$

In an ideal solvent at $\alpha = 1$ the intrinsic viscosity can be determined from the equation

$$[\eta] = KM^{1/2} \tag{15.23}$$

15.2.4. Effect of Molecular Mass and Molecular Shape of Polymer on Viscosity

The viscosity of dilute solutions is affected greatly by the molecular mass and molecular shape of the dissolved polymer. It follows from Eq. (15.21) that with increasing molecular mass of a polymer the intrinsic viscosity increases, i.e., the ordinate intercepts of the $\eta_{sp}/c = f(c)$ lines grow longer (Fig. 15.3). It is also evident from this figure that with increasing molecular mass of a polymer the slope of these lines increases.

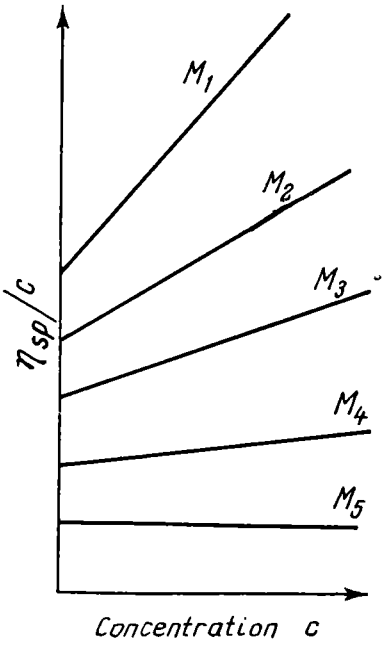

Fig. 15.3. Dependence of reduced viscosity of dilute solutions on concentration of polymers of different molecular mass ($M_1 > M_2 > M_3 > M_4 > M_5$)

Experiment shows that the slope is proportional to the square of intrinsic viscosity. Hence, Eq. (15.14) can be written as

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c \tag{15.24}$$

where k' is a constant.

Polyelectrolyte solutions are a good model for studying the effect of macromolecular shape on the viscosity of dilute solutions. The shape of a polyelectrolyte macromolecule can easily be changed by changing the degree of dissociation. Thus, polyacrylic or polymethacrylic acids are weakly dissociated in aqueous solution and contain a small number of charges along their chains, and therefore in dilute solution their chains curl up into coils, as has been proved by electron microscopy (Chap. 5). The sodium or potassium salts of these acids dissociate well, splitting off cations, so that a large number of negative charges form along their chains at fairly close spacing and electrostatic repulsion arises between these charges.

Electrostatic repulsion tends to straighten the chain, whereas thermal motion tends to coil it. If alkalis are added to the polyacids, there will be, for each pH value, an equilibrium between electrostatic repulsion and thermal motion, corresponding to a definite shape of the molecule. As the degree of dissociation increases, the molecules assume all the intermediate conformations from a random coil to a straight rod, as a result of which the specific viscosity of the polyacid solution increases with increasing pH by hundreds and thousands of times. Such a sharp increase in viscosity of the solution is due, first, to chain straightening, and, second, to interaction of the straightened-out chains with one another. Obviously, the higher the concentration of a solution, the greater this interaction should be. Therefore, the higher the concentration of a solution, the greater will be the increase of reduced viscosity with rising pH (Fig. 15.4).

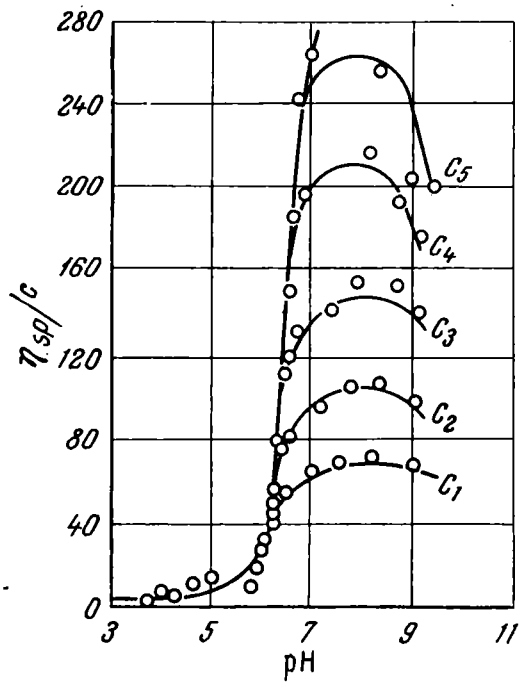

Fig. 15.4. Dependence of reduced viscosity of dilute polyacid solutions on degree of dissociation ($c_1 < c_2 < c_3 < c_4 < c_5$)

The viscosity of polyacid solutions rises with increasing pH up to a definite limit. After this, increase of pH decreases the viscosity because at certain pH values the concentration of ions in the solution increases sharply and they are attracted by the macromolecular ions. This causes screening of the chain charges, decreasing electrostatic repulsion and resulting in partial coiling of the macromolecules, and hence, in a decrease in viscosity of the solution.

15.2.5. Effect of Nature of Solvent on Viscosity of Dilute Solutions

Intrinsic viscosity and the slope of the η_{sp}/c vs. c line depend on the nature of a solvent. This is due to the fact that the coil swells differently in different solvents and therefore has different sizes. The volume of a swollen loose coil of spherical shape is much larger than the actual volume of the molecule regarded as the sum of volumes of its segments. When we speak of the size

of a molecule in a solution, we mean the size of this "effective" sphere, which depends on the thermodynamic affinity of a solvent, or its quality (p. 389).

It is the usual practice to study the size of molecules in ideal or θ-solvents (p. 437). The molecular size is then unperturbed by the solvent and can be estimated by its root-mean-square end-to-end distance $(\bar{r}_\theta^2)^{1/2}$. The relation between intrinsic viscosity and the size of an unperturbed coil has been shown theoretically to be

$$[\eta] = \Phi_0 \frac{(\bar{r}_\theta^2)^{1/2}}{M} \tag{15.25}$$

In a nonideal solvent the coil is α^3 times larger, i.e.,

$$(\bar{r}_\theta^2)^{1/2} = \alpha (\bar{r}_0^2)^{1/2} \tag{15.26}$$

Therefore for a nonideal solvent Eq. (15.25) becomes

$$[\eta] = \Phi_0 \frac{(\bar{r}_0^2)^{1/2}}{M} \alpha \tag{15.27}$$

Analysis of experimental data of $[\eta]$ and $(\bar{r}_\theta^2)^{1/2}$ measurement by light scattering of solutions led Flory to the conclusion that the parameter Φ_0 is a universal constant for all polymers. Depending on the units in which $[\eta]$ is expressed (ml/g or dl/g), Φ_0 equals 2.84×10^{23} or 2.84×10^{21}.

By means of Eqs. (15.25) and (15.27) the size of molecules in solution can be calculated from intrinsic viscosity measurements.

Since the coil swells differently in different solvents, it is interesting to relate intrinsic viscosity directly to the parameters of thermodynamic affinity of solvent for a polymer. This was first done qualitatively by Alfrey and Mark whose reasoning was approximately as follows: if the solvent interacts poorly with the polymer, polymer-polymer contacts are more probable, and therefore the chain will curl up. If the solvent interacts well with the polymer, polymer-solvent contacts will be more probable than polymer-polymer contacts and the chain will uncurl. A coiled chain offers less hydrodynamic resistance than an uncoiled one, and therefore the intrinsic viscosity of a polymer solution in a poor solvent is lower than in a good one.

To verify this assumption numerous studies were carried out in which $[\eta]$ values were compared for the same polymer in different solvents with thermodynamic interaction parameters such as $\Delta\mu_1$ or the second Virial coefficient. The experimental results show that in the case of flexible polymer chains there is a correlation between A_2 and $[\eta]$: the higher the thermodynamic affinity between a polymer and a solvent, i.e., the better the solvent, the higher will be the value of $[\eta]$. In the case of solutions of rigid-chain polymers

and especially of polymers with strong interchain interaction there is no such correlation, as has been shown convincingly by Frith, Moore and Howard *et al.* on solutions of cellulose derivatives.

Krigbaum suggested as semi-empirical relation between the osmotic second Virial coefficient A_2 and intrinsic viscosity:

$$[\eta] = [\eta]_\theta + 0.50 A_2 M \tag{15.28}$$

where $[\eta]_\theta$ = intrinsic viscosity measured in a θ solvent
M = molecular mass of a polymer.

It follows from the equation that the higher the value of A_2, the greater will $[\eta]$ be.

The most popular equation is that of Stockmayer and Fixman, derived for the intrinsic viscosity of flexible polymeric chains:

$$[\eta] = K_\theta \cdot M^{1/2} + 0.51 \Phi_0 B M \tag{15.29}$$

where K_θ = constant determined in the θ-solvent
M = molecular mass of a polymer
Φ_0 = universal viscosity constant
B = quantity related to the interaction parameter χ (p. 422) by the equation

$$B = v_{sp}^2 (1 - 2\chi)/V_1 N_A \tag{15.30}$$

where v_{sp} = specific volume of a polymer
V_1 = mole volume of a solvent
N_A = Avogadro's number.

With the aid of Eq. (15.29) the values of K_θ and B can be calculated on the basis of the graphical dependence $[\eta]M^{1/2}$ vs. $M^{1/2}$, the former from the ordinate intercept of the line, and the latter from its slope. Using Eq. (15.30), the interaction parameter χ can be calculated directly from viscometric data.

The interaction of a polymer with a solvent affects not only the intrinsic viscosity, but also the concentration dependence of the reduced viscosity, expressed by Eq. (15.24). This equation contains the parameter k', which has been shown experimentally to have different values for solutions in good and poor solvents. The parameter k' is known as Huggins' viscometric constant. In the case of flexible chain polymers a correlation was found between the values of k' and the parameters of thermodynamic interaction, e.g., A_2, namely: the higher the value of A_2, i.e., the better the solvent in the thermodynamic sense, the smaller will be the value of k' that can be determined from the slope of the η_{sp}/c vs. c line. On the other hand, high k' values are characteristic of poor solvents.

Correlation between the quantities k' and A_2 is observed only in the case of flexible chain polymers, and is not observed in polymers with rigid chains and strong specific interaction.

As has already been indicated, the sizes of unperturbed coils should be determined in a θ-solvent, i.e., in a solvent for which $A_2 = 0$. Very often binary liquid mixtures are used rather than individual liquids as θ-solvents, and it is therefore interesting to

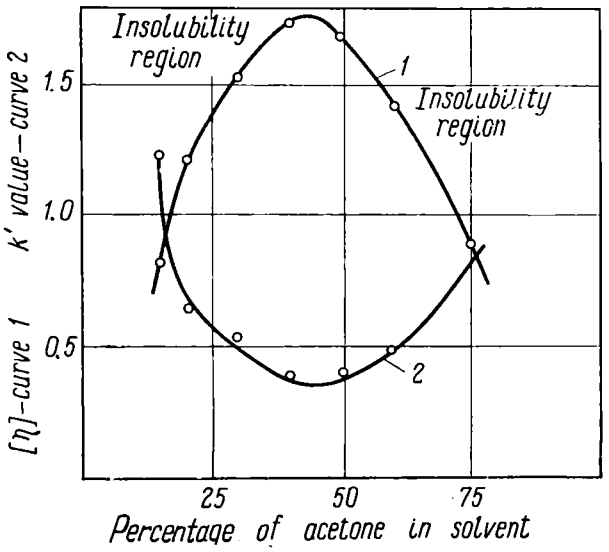

Fig. 15.5. Intrinsic viscosity (curve *1*) and Huggins' value k' (curve *2*) of a polystyrene fraction vs composition of the solvent mixture (acetone-methylcyclohexane), in each component of which the polymer is completely insoluble

establish how intrinsic viscosity varies depending on the composition of a binary mixture. Such studies were first made by Palit, Colombo and Mark for a solution of polystyrene in a mixture of acetone and methylcyclohexane. Their data are shown in Fig. 15.5. It can be seen distinctly from this figure that [η] varies with binary mixture composition along a curve with a maximum, and the Huggins constant k', along a curve with a minimum. The authors showed that the osmotic pressure of the solution and its turbidity vary extremally depending on the amount of acetone. The minimum on the [η] dependence curve corresponds to the highest value of osmotic pressure (lowest value of χ) and to minimum turbidity. All this is evidence that the maximal solubility of a polymer in a binary mixture corresponds to the maximum value of [η], i.e., in this case too, the better the solvent, the higher will [η] be.

In recent years many investigators have demonstrated experimentally the extremal dependence of [η] on binary mixture composition, maxima being observed on the curves in some cases and

minima in others. This means that the difference between the measured value of $[\eta]$ and its additive value, i.e., that obtained from the values of $[\eta]_1$ and $[\eta]_2$ measured in the pure solvents:

$$\eta_{ad} = \varphi_1 [\eta]_1 + \varphi_2 [\eta]_2 \tag{15.31}$$

where φ_1 and φ_2 are the volume fractions of both solvents in the binary mixture, may be positive or negative.

Theoretically this question was examined by Patterson, Dondos, and Benoit. The authors proceed from a simple model of a ternary solution corresponding to complete absence of predominant adsorption of one of the mixture components by the polymer. For such a model the following equation is valid:

$$\chi = r_1\chi_{13} + r_2\chi_{23} - r_1 \cdot r_2\chi_{12} \tag{15.32}$$

where r_1 and r_2 = mole fractions of solvents in binary mixture
χ = interaction parameter of polymer with dissolving mixture
χ_{13} = interaction parameter of polymer (3) with solvent (1)
χ_{23} = interaction parameter of polymer (3) with solvent (2)
χ_{12} = interaction parameter of solvents with each other, related to their excess free energy of mixing G^E by the equation

$$r_1 \cdot r_2 = \frac{G^E}{RT} \tag{15.33}$$

The authors show theoretically that the decisive parameter is χ_{12}, the sign of which coincides with that of G^E. Thus, if two solvents interact poorly with each other, i.e., if their mixture displays positive deviations from ideality ($G^E > 0$), then, according to Eq. (15.33), $\chi_{12} > 0$. This results in the solvents mixing with a polymer better than with each other, and the coil swells more than might have been expected from the thermodynamic interaction of each solvent with a polymer, and $[\eta]$ varies along a curve with a maximum.

If the solvents mix well with each other, i.e., their mixture shows negative deviation from ideality ($G^E < 0$ and $\chi_{12} < 0$), the solubility of a polymer in their mixture will grow worse, the coil will swell less than might have been expected and $[\eta]$ will vary with the composition of the dissolving mixture along a curve with a minimum.

Thus, theory predicts that the signs of the parameter χ_{12} and the difference $\Delta[\eta]$ will be the same, and this is confirmed by experiment. However, the authors point out that the correlation

between these values is only of a qualitative, rather than quantitative, nature owing to selective adsorption of one of the mixture components by the polymer chain.

15.2.6. Effect of Temperature on Intrinsic Viscosity

Intrinsic viscosity can increase or decrease together with temperature. This is directly connected with the temperature coefficient of the thermodynamic affinity of a solvent for a polymer, especially with the temperature coefficient of the second Virial

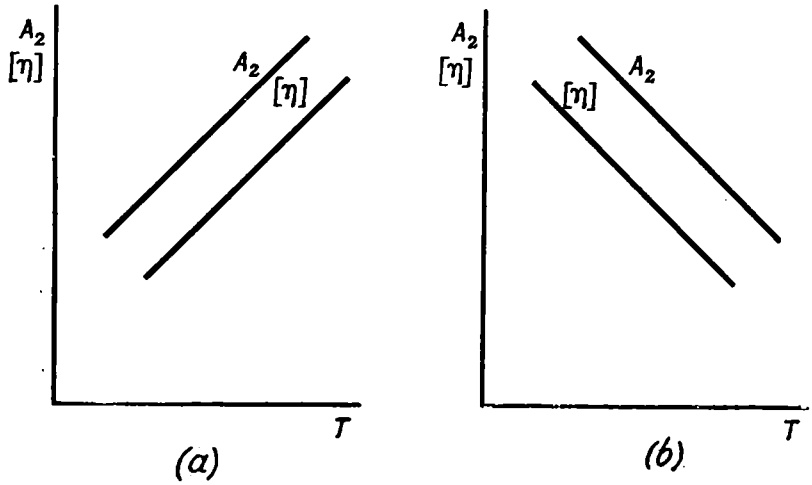

Fig. 15.6. Temperature dependence of $[\eta]$ and A_2 for a system having UCST (*a*) and a system having LCST (*b*)

coefficient, as is illustrated in Fig. 15.6. If thermodynamic affinity improves as temperature rises (A_2 increases), the coil swells more, and $[\eta]$ increases with an elevation of temperature. This is characteristic of systems possessing UCST (p. 404). If A_2 decreases as temperature rises, the coil swells less, and $[\eta]$ diminishes with an elevation of temperature, as is the case with systems possessing LCST. If A_2 changes extremely with temperature, i.e., if a system possesses both UCST and LCST, the coil contracts when temperature either rises or drops, and $[\eta]$ changes extremely with temperature.

15.3. CONCENTRATED POLYMER SOLUTIONS

Solutions are usually called *concentrated* if the solute molecules in them interact with one another. In polymer solutions this interaction sharply increases the viscosity compared to that of the pure solvent. Ferry suggests applying the term "concentrated" to polymer solutions with a relative viscosity of the order of at least

100. The lower limit of polymer concentration in them may vary from a fraction of a per cent for long rigid chains to 10 per cent for flexible polymers of low molecular mass; the upper limit is the undiluted polymer. Concentrated solutions are conventionally subdivided into moderately concentrated and highly concentrated solutions. The latter include solutions containing a volume fraction of a polymer of about 0.3 or more. They also include plasticized systems.

As to the problems associated with the processing of polymers and their concentrated solutions, the study of their rheological properties has aroused increasing interest. The study of the elasto-viscous properties of concentrated polymer solutions is important not only for practice, but can also yield valuable information concerning the structure of polymer solutions, which is represented as a spatial fluctuational network formed by more or less densely packed aggregates, or associates of macromolecules, and solvent molecules are distributed in it (p. 531). The main structural elements of such a network are free volume, i.e., volume unoccupied by the mass of a polymer and a solvent (p. 164), and the density and order of aggregates which constitute the network.*

There are two processes in deformation: (1) the fracture of the fluctuational network and aggregates, and (2) straightening out of macromolecules, which determines highly elastic deformation. If the energy of the mechanical field is commensurable with that of thermal motion, or if the deformation rate is small, structural changes will also be small, and they are recovered by thermal motion. Therefore, the structure of a solution prior to and after flow is practically the same. In this sense, it is usually said that the initial Newtonian viscosity η_{in}, measured at low σ_t and γ, reflects the flow of a solution having an unchangeable structure. The stronger the structure and the more ordered it is the greater is η_{in}. Therefore, it is very important to know the effect of various factors on η_{in}.

15.3.1. Initial Newtonian Viscosity of Concentrated Polymer Solutions

Effect of Concentration. The viscosity of solutions of flexible-chain polymers, which are in a rubber-like state under the conditions of an experiment, can be measured in the entire concentration rage, i.e., from a pure solvent to a pure polymer (Figs. 15.7, 15.8). The viscosity of glassy-polymer solutions in a very high concentration range sharply grows with concentration as the polymer-solvent system approaches a glassy state. Therefore, measure-

* Details on the structure of solutions are given in Chap. 17.

ments can be taken only up to a volume fraction of a polymer approximately equal to 0.8. When concentrations are sufficiently high, the viscosity of a polymer solution is proportional to φ_2^5 and even φ_2^{11}-φ_2^{17}. The relative viscosity of a solution also grows very sharply. Therefore, Eq. (15.24) cannot be used even for moderately concentrated polymer solutions, whose concentration dependence of viscosity is described by Martin's equation:

$$\frac{\eta_{sp}}{c} = [\eta] \exp(K_M [\eta] c) \quad (15.34)$$

where c = concentration in g/ml

K_M = Martin constant.

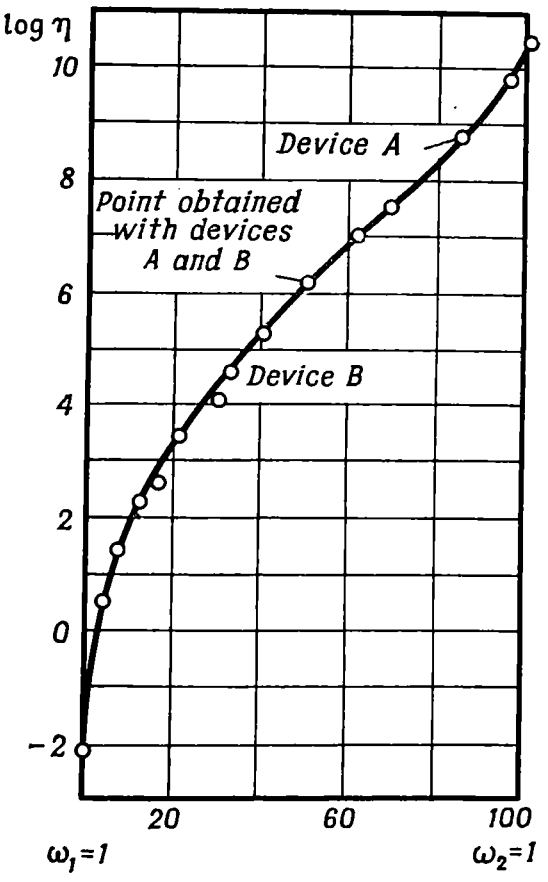

Fig. 15.7. Dependence of the logarithm of viscosity on composition for the polyisobutylene-toluene solution (at 20 °C)

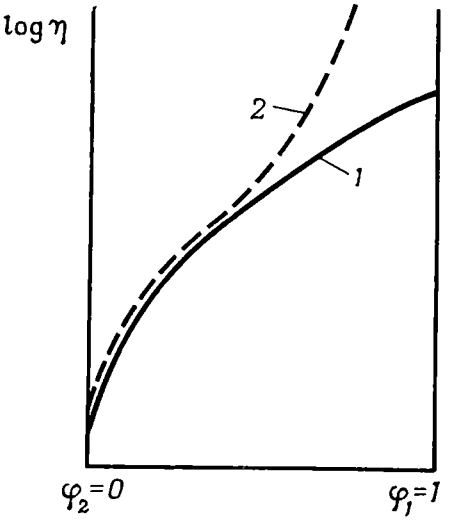

Fig. 15.8. Concentration dependence of maximum Newtonian viscosity: 1—for solutions of elastic polymers; 2—for solutions of glassy polymers

However, this equation also is valid only up to a concentration of 10-12 per cent.

The behaviour of polymer solutions in a wide concentration range was considered from the standpoint of various theories, which can be conditionally divided into two groups: theories based on the concept of the existence of molecular coils in the entire concentration range in a solution, that act as independent units (approach from the standpoint of dilute solutions), and theories based on the concept of the fluctuational network and free volume (approach from the standpoint of melts).

Equations based on the first type of concepts are valid only for flexible-chain polymer solutions at comparatively low concentrations. Equations based on the concept of free volume give a better description of the concentration dependence of viscosity of polymer solutions. Two of them are given below. One of them, suggested by Fujite and Kishimoto, is

$$-\frac{1}{\ln a_c} = f(T, \varphi_1^*) + \frac{f(T, \varphi_1^*)}{\beta'(T)} \cdot \frac{1}{\varphi - \varphi_1^*} \tag{15.35}$$

where

$$a_c = \frac{\eta(T, \varphi_1)(1 - \varphi_1^*)}{\eta(T, \varphi_1^*)(1 - \varphi_1)} \tag{15.36}$$

where $\eta(T, \varphi_1)$ and $\eta(T, \varphi_1^*)$ = viscosity coefficients of solutions with volume fractions of solvent φ_1 and φ_1^* at temperature T, the latter solution being the standard

$f(T, \varphi_1^*)$ = relative free volume of solution of standard concentration

$\beta'(T)$ = interaction function of solvent with polymer.

It follows from Eq. (15.35) that the dependence $1/\ln a_c = f[1/(\varphi_1 - \varphi_1^*)]$ should be represented by a straight line, from the slope of which the value of $\beta'(T)$, and from the ordinate intercept of which the value of $f(T, \varphi_1^*)$, can be determined. The standard state may be a solution of any concentration or the pure polymer ($\varphi_1^* = 0$).

Equation 15.36 has been verified for many polymer-solvent systems and good agreement with experiment has been obtained, especially for solutions with $\varphi_2 < 0.5$.

A second equation relating the viscosity of a polymer solution to its concentration was derived by Bueche and Kelley. The authors proceed from the idea of additivity of the free volumes of a polymer f_p and a solvent f_s and make use of Eq. (8.1) (see Chap. 8):

$$f_p = \frac{V_{f2}}{V} = 0.025 + 4.8 \times 10^{-4}(T - T_g) \tag{15.37}$$

$$f_s = \frac{V_{f1}}{V} = 0.025 + \alpha_s(T - T_g') \tag{15.38}$$

where 0.025 = relative free volume of substance at glass-transition temperature (p. 210)

$4.8 \times 10^{-4}\ \text{deg}^{-1}$ = thermal expansion coefficient of polymer

α_s = thermal expansion coefficient of solvent which for liquids is of the order of 10^{-3} deg^{-1}

T_g and T'_g = glass-transition temperatures of a polymer and a solvent.

Assuming additivity of free volumes, the authors obtained the following equation:

$$\ln \eta/B = 4 \ln d_2 \{\varphi_2 [0.025 + 4.8 \times 10^{-4} (T - T_g)] + (1 - \varphi_2)[0.025 + \alpha_s (T - T'_g)]\} \quad (15.39)$$

where d_2 = density or mass concentration of polymer in solution

φ_2 = volume fraction of polymer in solution

η = viscosity of solution

B = parameter depending on molecular mass of polymer.

This equation was verified for a number of systems (in particular, for solutions of polyisobutylene) and it was found that

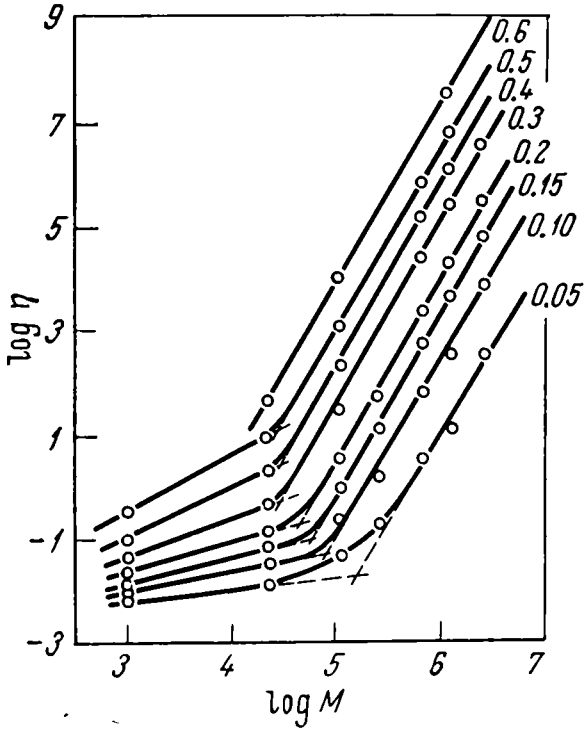

Fig. 15.9. Viscosity versus molecular mass for polyisobutylene solutions. The numbers on the curves are concentrations of solutions in volume fractions

theory agrees best with experiment at temperatures above the glass-transition temperature of the dissolved polymer. For polystyrene solutions at room temperature and for solutions of poly(methyl methacrylate) at 60 °C theory does not agree with experiment. This is due to the fact that actually free volumes are not strictly additive, and are the less so, the greater the contraction

that occurs when a polymer is mixed with a low-molecular liquid (p. 400). Dissolution of loosely packed glassy polymers involves more contraction than that of polyisobutylene.

Effect of the Molecular Mass of a Polymer. In recent years Ferry, and Bueche and coworkers have shown that for concentrated polymer solutions the log-log dependence of viscosity on degree of polymerization P is represented, as in the case of the polymers themselves, by two intersecting straight lines. With $P > P_{cr}$ the slope is 3.4 in all cases.

The log η vs. log P dependence has been studied by different researchers over a wide range of concentrations, and the relevant data are shown in Fig. 15.9. In accordance with Bueche's theoretical predictions, the intersections of the lines shift towards larger P_{cr} values as the concentration of the solution decreases. The product of critical chain length and concentration of solution $P_{cr}c$, however, remains approximately constant. It depends on the nature of the dissolved polymer: the more rigid the polymer chain, the smaller is $P_{cr}c$. Thus, for polyisobutylene solutions it equals 180, and for poly(vinyl alcohol) solutions it is 80. With rising temperature the product $P_{cr}c$ increases slightly. The constancy of this product signifies that the greater the chain length, the lower the concentration at which intensive structure formation begins in the solution.

15.3.2. Effect of the Quality of a Solvent on the Viscosity of Polymer Solutions

The viscosity of a polymer solution is determined not only by the volume fraction of a polymer, but also by the nature of a solvent. The viscosity of the latter and its thermodynamic affinity for the polymer, i.e., its quality, have their effect (p. 381). If two solvents, whose quality to a given polymer is similar, differ from one another by their viscosity, the viscosity of a solution in a more viscous solvent is always greater than that in a less viscous one. But this difference is not great comparatively, while the difference in the quality of a solvent can cause an astounding difference in the viscosity of a solution. In this case, the quality of a solvent is expressed the stronger, the more rigid is the chain and the greater is interchain interaction. This is clearly shown in Fig. 15.10, which illustrates the change in the relative viscosity of polymer solutions in good solvents as an increasing amount of poor solvents is added.

The viscosity of solutions of a very flexible-chain polymer, poly(dimethyl siloxane) (PDMS), diminishes practically in the entire concentration range as the quality of the solvent worsens, i.e., the same regularity as that for intrinsic viscosity is observed. The

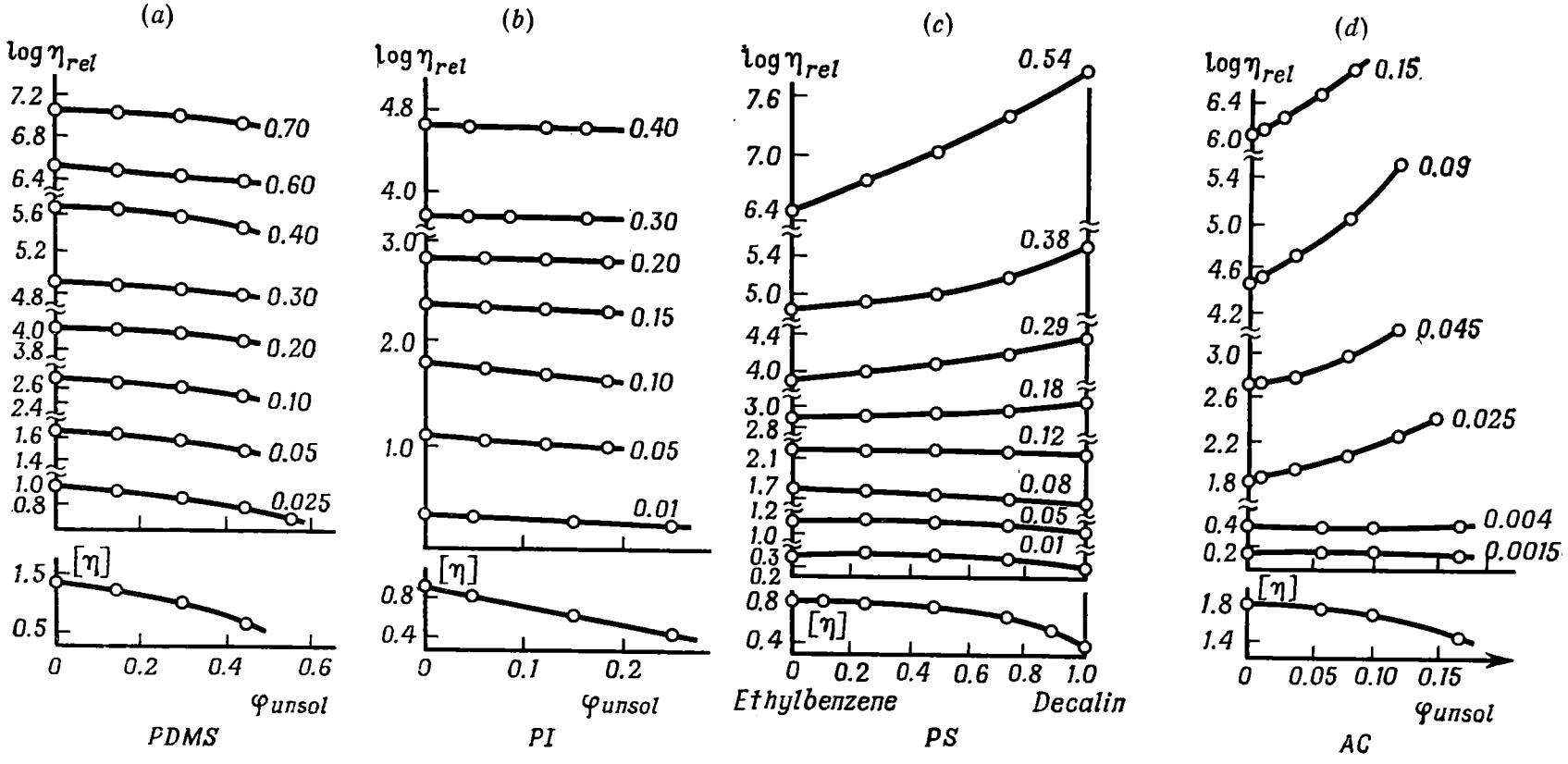

Fig. 15.10. Dependence of relative viscosity η_{rel} and $[\eta]$ of polymer solutions on the volume fraction of nonsolvent (or poor solvent) in a dissolving mixture. The numbers on the curves are volume fractions of polymers in solutions:
a—PDMS in a mixture of ethyl benzene and butanol; *b*—PIB in a mixture of carbon tetrachloride and isopropanol; *c*—PS in a mixture of ethyl benzene-decalin; *d*—AC in a mixture of trichloroethylene and octane

viscosity of polyisobutylene (PIB) and polystyrene (PS) solutions diminishes as a poor solvent is added only when their concentration is less than 0.15. The viscosity of PIB solutions of greater concentration does not depend on the quality of a solvent, while the viscosity of PS solutions grows the greater, the higher is the concentration of a solution, as the quality of a solvent worsens. The viscosity of the solution of a more rigid-chain and polar polymer, cellulose acetate, grows practically in the entire concentration range, beginning from very great dilutions, as the quality of a solvent worsens.

Viscosity diminishes as the quality of a solvent worsens, because macromolecular coils contract. However, this cannot explain why viscosity grows as the quality of a solvent worsens. This growth is due to the effect of a solvent on the degree of fracture of supermolecular polymer structures when the initial stage of polymer dissolution in good or poor solvents is concerned, or on the extent of aggregation of macromolecules when a poor solvent is added to a good one. Evidently, the better a solvent thermodynamically, the greater is its ability to loosen supermolecular structures in a polymer, and therefore the fluctuational network in a solution is not very dense (or loose). A poor solvent can penetrate only between some weak structural regions of a polymer, while strong regions remain unfractured. Therefore, the fluctuational network of a solution is dense, and this leads to higher values of viscosity.

Hence, the deterioration of quality of a solvent can affect the conformation of macromolecules and the extent of their aggregation. The former causes a diminution in viscosity, and the latter, its rise. If these effects are compensated, the viscosity of a polymer solution may be independent of the quality of a solvent. This is apparently observed for concentrated PIB solutions, whose viscosity does not depend on the quality of a solvent.

These data clearly show that the regularities observed in dilute solutions should be applied with great care to concentrated ones. This is quite inadmissible when solutions of moderately rigid or rigid-chain polymers are involved. In this case, the regularities observed in dilute and concentrated solutions are quite the opposite, i.e., intrinsic viscosity diminishes as the quality of a solvent worsens, while the relative viscosity of concentrated and even moderately concentrated solutions grows. Therefore, the viscosity of concentrated solutions of such polymers in poor solvents is always greater than in good ones, and the difference between them may be as much as three or four decimals. Thus, the viscosity of equiconcentrated PS solutions in a poor solvent, decalin, is greater than in a good one by 100-1000 times, while that of acetate (AC) solutions in a poor solvent is greater than in a good

one by 10 000 times (Fig. 15.11). It follows that even very small additions of good solvents to solutions of polymers in poor solvents can reduce viscosity by tens of times.

The introduction of small additives of some substances into polymer melts can also cause a sharp diminution in viscosity. This was observed by Natov and his coworkers when a series of aromatics was added to a polyethylene melt. V. A. Kargin and

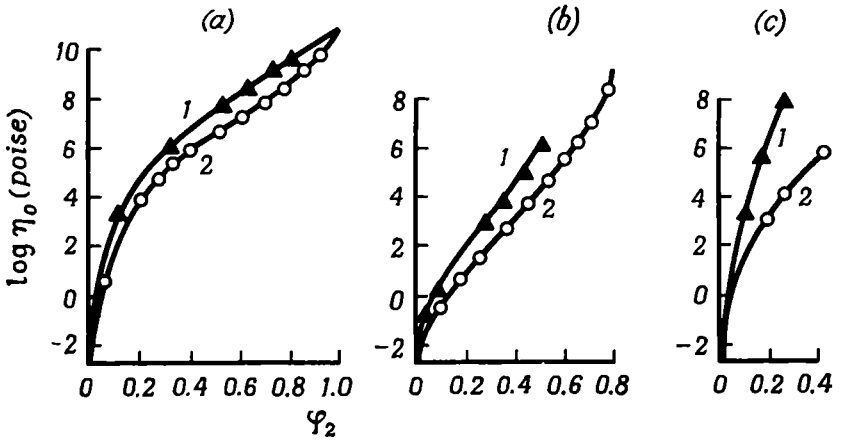

Fig. 15.11. Concentration dependence of viscosity for solutions of PIB (*a*) PS (*b*) and AC (*c*) in poor (*1*) and good (*2*) solvents

G. P. Andrianova have shown that the viscosity of a polypropylene melt can be reduced by 30-40 times by introducing small amounts of some oligomers.

Conversely, additions of small amounts of poor solvents to polymers can cause the formation of a system whose viscosity is greater than that of the polymer. This was first observed when very small amounts of chlorinated paraffin and oligomeric polyvinyl chloride were added to a polyethylene melt. Viscosity grows when microquantities of oligoether acrylates are added to СКИ-3 rubber. These phenomena are closely connected with interstructural plasticization (p. 557).

Hence, by using solvents and plasticizers having different thermodynamic affinity for polymers, we can control their viscosity and, consequently, the structure of solutions and plasticized systems.

15.3.3. Effect of Temperature on the Viscosity of Concentrated Polymer Solutions

The absolute values of the Newtonian viscosity of polymer solutions diminish with a rise in temperature, as is the case with low-molecular liquids, and this is usually connected with the

structural change of a liquid that occurs under the action of thermal motion.

Two factors operate in solutions, unlike in pure liquids: an increase in the intensity of thermal motion and a change in the quality of a solvent with temperature. The first factor should always cause a diminution of viscosity as temperature rises, while

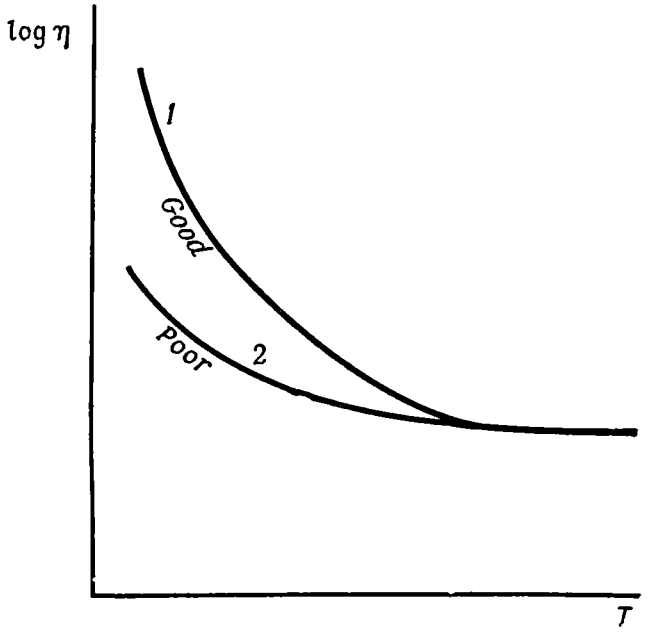

Fig. 15.12. Temperature dependence of η_{sw} for solutions of polymers in good and poor solvents (scheme)

the quality of a solvent changes differently with temperature (Chap. 12).

An improvement in the quality of a solvent with a rise in temperature promotes the structural disintegration of the solution, and, consequently, produces the same effect as thermal motion. Therefore, viscosity diminishes quite sharply as temperature rises. This is valid for solutions of polymers in poor (at room temperature) solvents, which become better on heating (curve *1*, Fig. 15.12). If the quality of a solvent worsens as temperature rises, then, conversely, the structure does not disintegrate, but originates on heating, and this weakens the action of thermal motion. Therefore, in the second case, the viscosity of a solution should change less sharply with temperature than in the first case, and this is observed in reality (curve *2*, Fig. 15.12). If, for example, the viscosity of a solution of a polymer in a poor solvent at room temperature was much higher than in a good one, these solutions can possess the same viscosity at a certain temperature, i.e., the difference in the viscosity of solutions in poor and good solvents always levels out as temperature rises.

Hence, in considering the effect of temperature on the viscosity of polymer solutions, it should be borne in mind that viscosity depends on the change in the quality of a solvent as temperature changes. In definite ranges of temperatures characteristic of every polymer [usually, it is the range of temperatures which are close to the high-temperature binodal (p. 391)], the intensive structure formation of a solution can cause an increase in viscosity as temperature rises.

The temperature dependence of viscosity is expressed by the Frenkel-Eiring equation:

$$\eta = A \cdot e^{\Delta G_v/RT} \tag{15.40}$$

where G_v = free activation energy of the flow process connected with the heat and entropy of activation by the thermodynamic relationship $\Delta G_v = \Delta H_v - T\Delta S_v$.

The calculation of activation parameters is always hampered by the indeterminacy of the pre-exponential term. But it is considerably simplified if we proceed from the conception proposed by Kobeko that the quantity in the exponent of such an equation has the meaning of the activation energy of a process if the pre-exponential term has a physical meaning.

Let us consider the physical meaning of A in Eq. (15.40). Evidently, A has the dimension of viscosity, since the term $e^{\Delta G_v/RT}$ is dimensionless. It is the viscosity of a substance at very high temperature when $e^{\Delta G_v/RT} \to 1$. Kobeko, Shishkin and Gurevich have shown that as temperature rises and approaches T_{boil}, the viscosity of all liquids tends to 10^{-3} poise. At temperature higher than T_{boil}, the liquid becomes a gas, but the viscosity of gases at high temperature also tends to the quantity of 10^{-2}-10^{-3} poise. The viscosity of plasma also tends to this quantity. Consequently, the quantity is characteristic of any substances, and the relaxation time $\tau = 10^{-12}$-10^{-13} s corresponds to it. It is viscosity which conforms to the thermal vibrations of atoms.

Hence, Kobeko is correct in assuming that the pre-exponential factor in Eq. (15.40) should be the same for all substances, and should not depend on their nature.

If we take $A = 10^{-3}$ poise, the calculation of activation parameters is simplified. Eq. (15.40) assumes the following form:

$$\Delta G_v = 2.303\ RT \log \frac{\eta}{10^{-3}} \tag{15.41}$$

$$\log \eta = \left(\log 10^{-3} - \frac{\Delta S_v}{R}\right) + \frac{\Delta H_v}{R} \cdot \frac{1}{T} \tag{15.42}$$

Equation (15.41) can be used to calculate the value of ΔG_v when the viscosity of a solution is known; the graphically plotted dependence of the logarithm of viscosity on inverse temperature

can be used to calculate the heat of activation, and the difference of these two quantities can be used to calculate the entropy of activation of viscous flow.

The parameters of activation of viscous flow are very sensitive to the structure of a solution: the heat of activation of flow gives information on the strength of the structure, while the entropy of activation, on its order.

For example, solutions of polymers having not very strong and poorly ordered structures are characterized by low values of heats

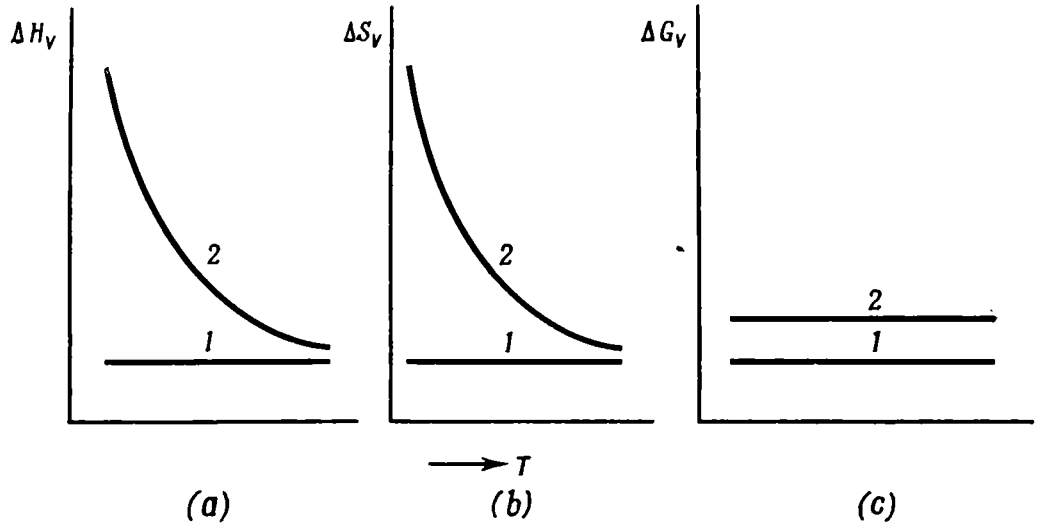

Fig. 15.13. Temperature dependence of heat (*a*), entropy (*b*) and free energy (*c*) of activation of flow:
1—poorly crosslinked polymer systems; *2*—highly crosslinked systems

and entropies of activation of flow and their unchangeability in a wide temperature range (Fig. 15.13). This is observed for solutions of polyisobutylene in all liquids in which it dissolves generally, for solutions of other flexible-chain polymers and also for solutions of PS in good solvents. High values of heats and entropies of activation of viscous flow and their sharp diminution with a rise in temperature gives information on sufficiently strong and ordered structures of a system, which is characteristic of, say, cellulose acetate solutions. In this case, the effect of compensation of heat and entropy of activation is observed; this effect was first detected by Ginshelwood for chemical reaction. Therefore, the free energy of activation, which determines the viscosity of a system, is not dependent on temperature.

The division of the free energy of activation of flow into the heat and entropy of activation helps also to understand the causes of a sharp growth in viscosity with the molecular mass of the polymer. In the high molecular mass region, the heat of activation

practically does not depend on the molecular mass (Fig. 15.14), and therefore it is not clear why viscosity grows so sharply. This is due to a considerable change in the entropy of activation, as a result of which the free energy of activation also grows (Fig. 15.14). In this case, the entropy of activation can be either positive or negative, and this reflects the mechanism of the flow process and the processes which are connected with it. For example, if the process of fracture of a solution structure prevails, the system becomes less ordered whenever there is flow, and this is accompanied with a positive value of the entropy of activation. If the process of the uncoiling and orientation of macromolecules prevails, as is characteristic of, say, the flow of high-molecular PIB, the system becomes more ordered in the course of flow and the entropy of activation is negative.

As the molecular mass of a polymer diminishes, the extent of coiling of its molecules decreases (Chap. 4), and the orientational effect is expressed less: the quantity ΔS_v becomes less negative and changes the sign.

The effect of temperature, the nature of a solvent, shear stress and concentration on the viscosity of concentrated polymer solutions are compensated, i.e., the superposition of all these effects is observed. By varying all these parameters, the same value of viscosity of a polymer solution can be obtained. This is used in practice to prepare, for instance, spinning solutions.

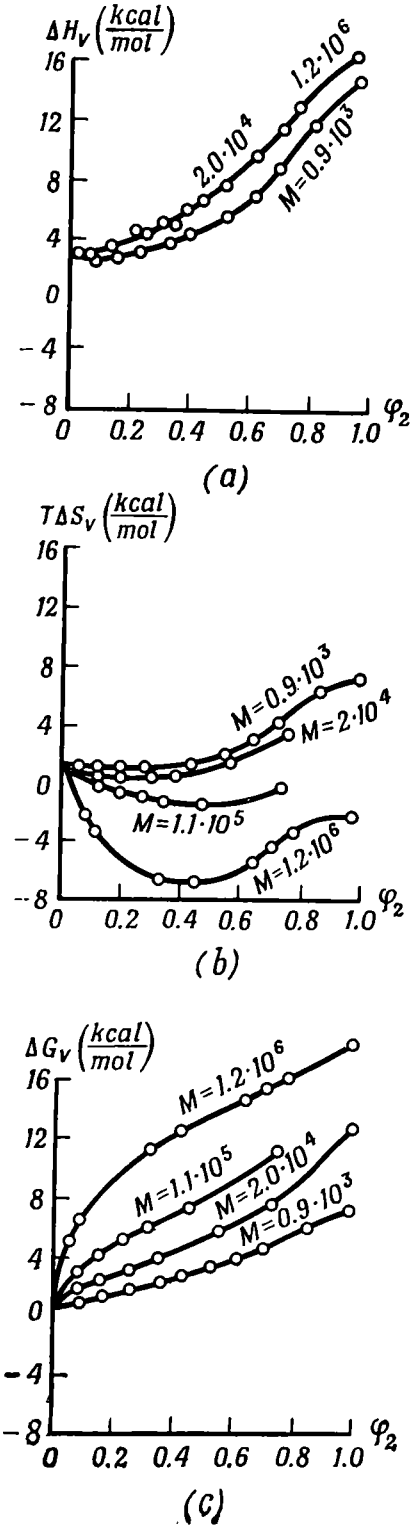

Fig. 15.14. Concentration dependence of heat (*a*), entropy (*b*) and free energy (*c*) activation of flow for a solution of polyisobutylene in isooctane. The numbers on the curves are molecular masses of polymers

15.3.4. Effect of the Quality of a Solvent on the Shear Modulus of Elasticity

The effect of the quality of a solvent on the shear modulus of elasticity of polymer solutions also depends on the nature of the polymer chain. For example, the quality of a solvent does not effect the magnitude of the elasticity modulus in respect of solutions of a flexible-chain polymer, PIB, and even for PS solutions. The elasticity modulus for solutions of poly(methyl methacrylate) and cellulose acetate, i.e., polymers of greater polarity, in poor solvents is higher than for solutions in good solvents. But the magnitudes of moduli differ considerably less than that of viscosity. Consequently, the elasticity modulus is less sensitive than viscosity in respect of the quality of a solvent, because the viscosity of concentrated polymer solutions is determined mainly by the density of the fluctuational network and interchain interaction, while highly elastic deformation, by the flexibility of the polymer chain. Both of them depend on the quality of a solvent (p. 389). But apparently the quality of a solvent has a considerably greater effect on the density of a network than on chain flexibility, especially when polymers having great equilibrium flexibility are concerned. For moderately rigid polymers, chain flexibility apparently depends to a greater extent on the quality of a solvent, and this affects the magnitude of the elasticity modulus. The latter changes very sharply depending on the quality of a solvent for the gels of gelatin, whose macromolecules are very rigid.

15.3.5. Viscosity Anomaly

At high stresses and rates of shear, structural changes in polymer solutions are very great, and they are not recovered by thermal motion. Therefore, the viscosity of a solution greatly changes, and is the function of stress and rate of shear, i.e., viscosity anomaly is observed (Chap. 10).

Changes in the solution structure are expressed in the fracture of the existing network and in the origination of new structural formations due to the straightening out of macromolecules and their mutual orientation. Therefore, the viscosity of a solution can decrease, increase or remain unchanged as shear stress grows. This depends on the concentration of a solution, temperature, the quality of a solvent, the nature of a polymer chain, molecular-mass distribution, and the conditions of deformation.

Under shear deformation, a decrease in the viscosity of a solution is mostly observed as shear stress grows. Incomplete flow curves are observed for dilute solutions of all polymers. As we

have already seen, effective viscosity is due to the orientation of macromolecules in flow, and the attained values of the minimum Newtonian viscosity is connected with maximally oriented chains (p. 468).

The shape of flow curves of polymer solutions of greater concentration depends on the nature of a chain. For example, the third region degenerates on the flow curves of flexible-chain polymer

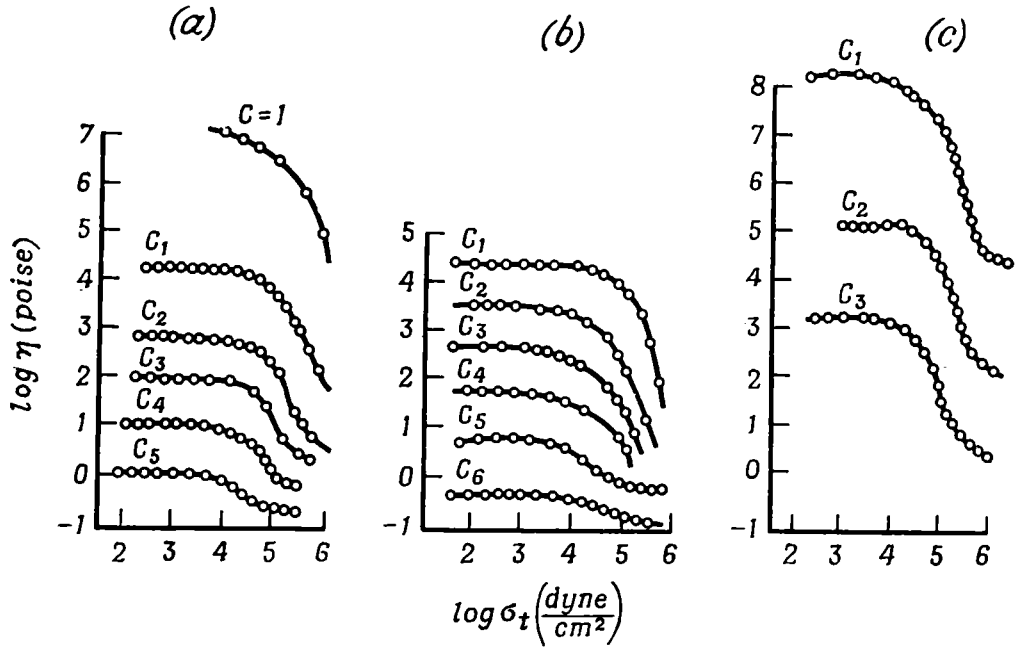

Fig. 15.15. Flow curves of solutions of polyisobutylene (*a*); polystyrene in a good solvent (*b*) and cellulose acetate (*c*) at different concentrations

solutions as concentration grows, and a single inflection point is observed; then, this point also disappears, and only two regions remain, as is the case with melts (Fig. 15.15*a*). The reasons why the third region is not attained are given on page 458. Such a nature of flow is maintained in a wide temperature range and is independent of the solvent quality, which does not affect the value of effective viscosity as well (Fig. 15.15*b*).

Complete flow curves are observed for rigid-chain polymer solutions, e.g., solutions of AC and other cellulose esters, at all temperatures and in all solvents. In the presence of such rigid chains, diminutions of viscosity can hardly be explained by the straightening out of macromolecules. This is apparently due to the fracture of the fluctuational structural network. But it seems that a part of stronger structures cannot be fractured by shear stress applied, and this explains the presence of the third region, which conforms to flow with the minimum Newtonian viscosity.

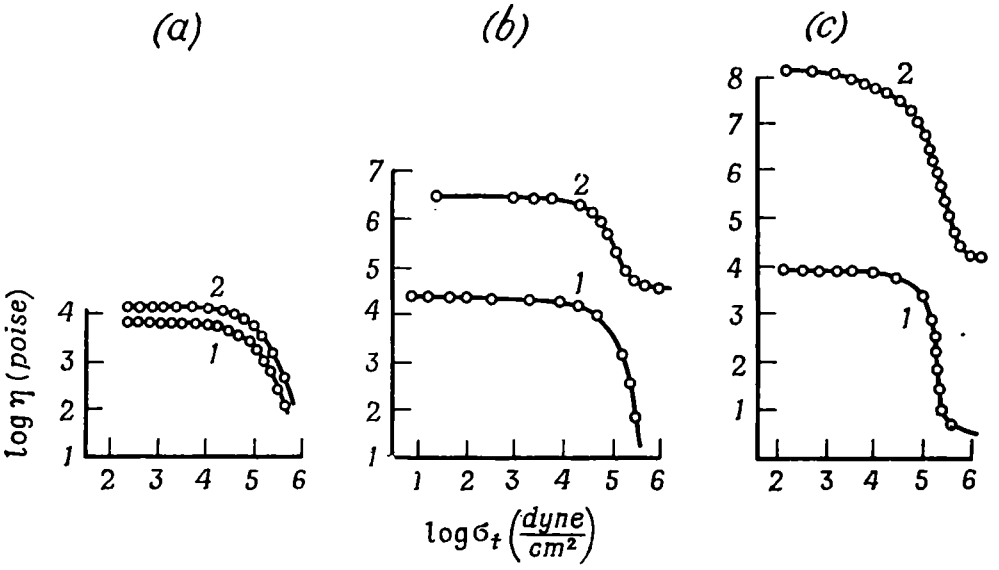

Fig. 15.16. Flow curves on concentrated solutions of polyisobutylene (*a*), polystyrene (*b*) and cellulose acetate (*c*) in good (*1*) and poor (*2*) solvents

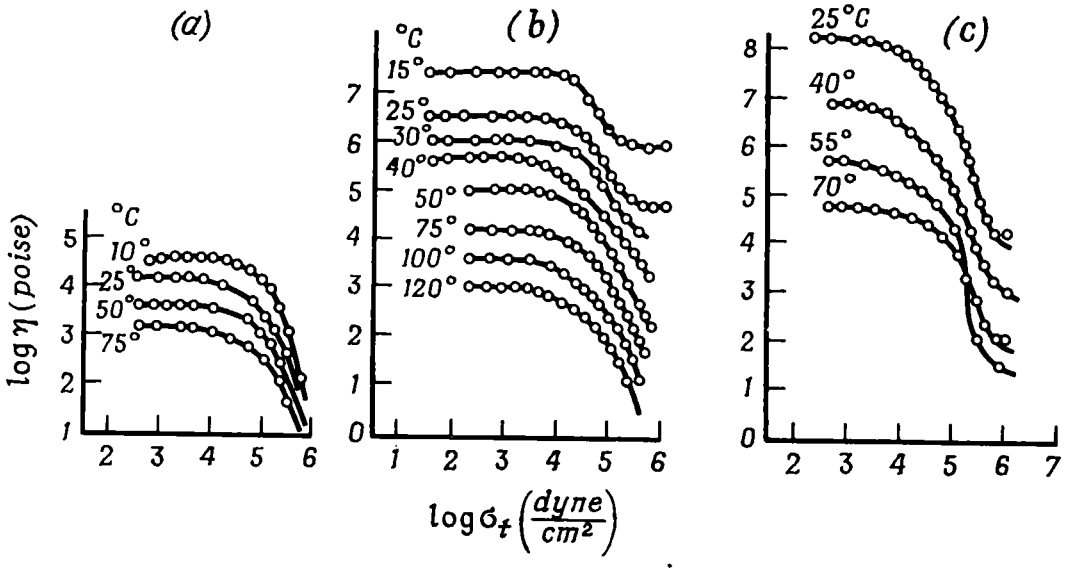

Fig. 15.17. Flow curves of solutions of polyisobutylene (*a*), polystyrene in poor solvent, i.e., decalin (*b*) and cellulose acetate (*c*), at various temperatures

This explanation is underpinned by two facts:

1. Even when dilutions are very high, unfractured associates remain in the solutions of AC and other polar polymers, and this is expressed in higher values of molecular masses.

2. Complete flow curves are also observed for solutions of PS in poor solvents (Fig. 15.16), and the third region disappears at elevated temperature or when a good solvent is added (Fig. 15.17),

i.e., under these conditions, the formerly intact structures are fractured.

Viscosity anomaly is expressed always the stronger, the wider is the molecular-mass distribution, and it is not observed for concentrated solutions of monomolecular flexible-chain polymers. Such systems act in the same way as melts (p. 158). In the course of dilution, a deviation from Newton's law is observed even in respect of monomolecular polymers.

15.4. INVARIANT REDUCTION METHODS

It follows from the material expounded on page 469 that at present there is no theory of viscosity of polymer solutions which would make it possible to obtain an equation that satisfactorily

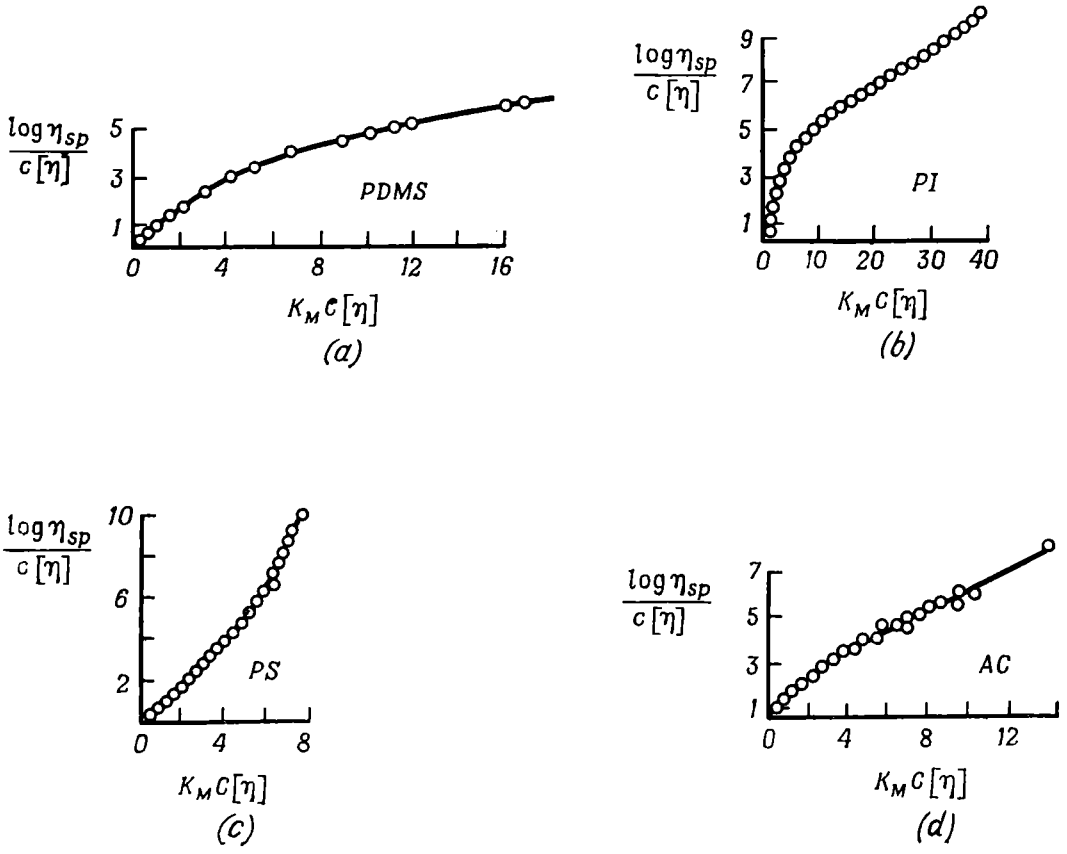

Fig. 15.18. Viscosity of solutions of polydimethyl siloxane (*a*), polyisobutylene (*b*), polystyrene (*c*) and cellulose acetate (*d*) in the given coordinates in various solvents

describes the flow of concentrated polymer solutions. Therefore, many endeavours are being made to compare the viscosity of polymer solutions at different concentrations, temperatures, molecular masses of polymers, and so forth, in reduced quantities. The

reduction method was used by Buecke, Simha and many other researchers for the Newtonian flow of polymer solutions. Intrinsic viscosity is taken as the normalizing parameter, or the reduction parameter. At first, attempts were made to represent the concentration dependence of the viscosity of polymer solutions in the coordinates $\frac{\eta_{sp}}{c[\eta]}$ vs. $c[\eta]$. But this did not lead to the coincidence of curves in the entire concentration region. Later, instead

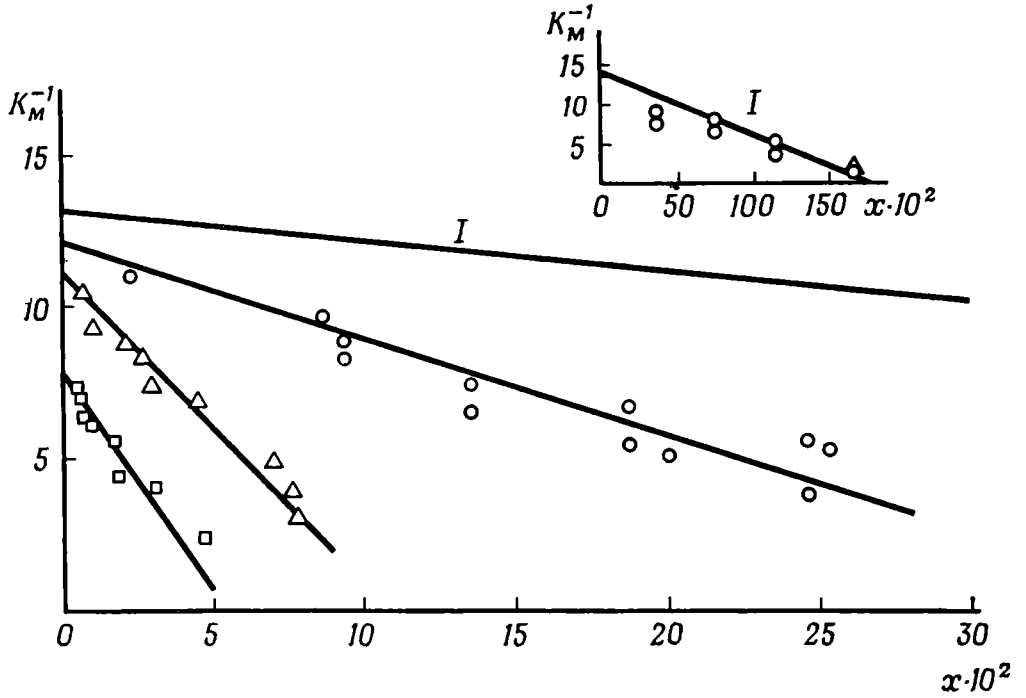

Fig. 15.19. Dependence of the quantity inverse to the Martin constant on the Flory-Huggins interaction parameter:
I—PDMS; ○—PIB; △—PS; □—AC

of the parameter $\frac{1}{[\eta]}$, Simha and coworkers proposed that the empirical parameter γ should be taken, which is a shear factor of curves prior to their superposition. However, in this case, concentration curves of polymer viscosity in different solvents cannot be made to coincide.

Such a coincidence turns out to be possible if experimental data are presented in the coordinates $\frac{\eta_{sp}}{c[\eta]}$ vs. $K_M c[\eta]$, where K_M is the Martin equation constant (p. 469). As Fig. 15.18 shows, the concentration dependence of viscosity of every polymer in various solvents is expressed by a single curve, which can be used to calculate the viscosity of a solution of this polymer at any concentration in any solvent. For this purpose, only the intrinsic viscosity of this solution should be measured experimentally.

The Martin constant expresses the slope of the curve of dependence of reduced viscosity of a solution on concentration, as determined by interchain interaction, i.e., by the extent of aggregation of macromolecules. Hence, the parameter $[\eta]$ takes account of the effect of a solvent on the size of a molecular coil, while the parameter K_M, on the extent of aggregation. The quantity K_M in turn depends on the quality of a solvent (Fig. 15.19): as the quality of a solvent worsens, the quantity K_M and, consequently, the viscosity of a solution become greater. A change in K_M with a change in the quality of a solvent is more considerable, the more rigid is a polymer chain and the greater is interchain interaction.

15.5. RHEOLOGICAL PROPERTIES OF POLYMER GELS

The solution-gel transition, i.e., gelation, is always characterized by a very sharp growth of viscosity with time. This is due to the gradual formation of stronger crosslinks, which are not fractured by thermal motion and low shear stresses. However, gels differ from one another by their rheological behaviour, depending on the bonds formed, whether chemical or intermolecular ones.

First-Type Gels. They are systems with chemical crosslinks which are incapable of flowing. They can flow only at very high stresses, which fracture these crosslinks, i.e., which fracture the entire system. In this case, sections of the fractured structure move, i.e., *chemical flow* is observed. But under the action of very small normal and tangential stresses, the first type of gels are capable of undergoing very great reversible highly elastic deformations, whose quantities depend on the density of a network and the extent of swelling. Experiment shows that the extent of expansion of a gel decreases as the extent of swelling increases; in this case, the coefficient C_2 in the Mooney-Rivlin equation diminishes (p. 189). Therefore, the following equation is valid for this type of gels:

$$\sigma = \frac{dRT}{M_{gel}}\left(\lambda - \frac{1}{\lambda^2}\right)$$

According to the equation, the dependence between stress and the quantity $\left(\lambda - \frac{1}{\lambda^2}\right)$ should be expressed by a straight line from the slope of which, i.e., from the value of the elasticity modulus, we can calculate M_{gel}. At very small gel deformation, proportionality between σ and λ is observed.

The relationship between stress and strain of a gel is widely used to estimate the extent of crosslinking of spatially crosslinked polymers, which are studied in a swollen state.

The elasticity modulus thus determined and the value of stress increase in direct proportion to absolute temperature.

Second-Type Gels. Unlike polymer solutions at small shear stresses, the second type of gels do not reveal noticeable flow. Therefore, the absence of fluidity was long assumed to be generally the main indication of any gels; this was wrong, as subsequent researches have shown. The gels of second type are capable of flowing, but this occurs usually at a definite value of shear stress, below which gels act as solid elastic bodies, and above which, as flowing liquids. This shear stress became known as the *ultimate shear stress* (yield point), and its value was believed to

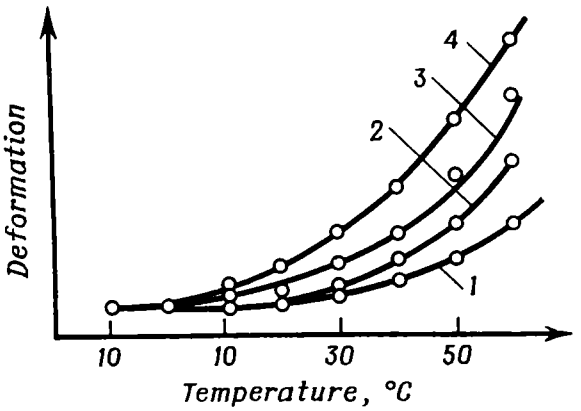

Fig. 15.20. Temperature dependence of compression strain for gelatin gels. The numbers on the curves are the logarithms of the frequency of the acting force

be connected with the strength of intermolecular bonds, which must be fractured. However, as we have seen in Chap. 9, bodies do not have an ultimate strength, and the destruction of a body is a process which occurs with time. This is also true of the second type of gels. Trapeznikov, for instance, believes that irrecoverable deformations in gels can develop at any stress, depending on the time that a gel is in a loaded state. The shape of the curves of low-concentrated gelatin gels is similar to that of the flow curves of concentrated solutions of rigid-chain polymers, i.e., there are three regions which correspond to Newtonian and non-Newtonian flow. In this case, the viscosity coefficient sharply grows as the quality of a solvent worsens.

The viscosity of a gel diminishes under the action of stress due to the disintegration of its structure, which is reversible in some cases, i.e., the system gelates again after stress is removed. Such gels possess *thixotropic* properties (p. 277). In some cases, an opposite phenomenon is observed, when the viscosity of a system grows under the action of shear stress and it gelates. When stress is removed, the gel reversibly melts. Such a system possesses *antithixotropic* properties. This is observed for systems of poly(methacrylic acid)-water, poly(methyl methacrylate)-dimethyl

formamide and others, and it occurs as the structure becomes ordered under the action of the mechanical field.

Owing to the presence of a spatial network of a non-fluctuational nature, the second type of gels are capable of undergoing very great recoverable highly elastic deformations, which are of a relaxational nature, i.e., the deformation depends equally on time and temperature (p. 218). This was shown for the first time by Kargin, Zubov and Zhurkina, and later by the other researchers. Figure 15.20 gives data to illustrate this. Highly elastic deformation of the second type of gels is of an energetic nature, i.e., it is connected with intermolecular interaction. Therefore, the shear modulus of such gels does not increase, but decreases with an elevation of temperature. It changes with the quality of a solvent to a considerably greater extent than the shear modulus of concentrated polymer solutions.

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CHAPTER 16

Determination of Molecular Mass of Polymers, Size and Shape of Macromolecules. Estimation of Thermodynamic Flexibility of a Chain

From what has been said in the previous chapters it follows that the properties of polymers are dependent on molecular mass. It is therefore necessary to have at our disposal methods of determining the molecular mass of polymers.

The most common thermodynamical methods of determining the molecular mass of substances, viz., cryoscopy and ebulliometry, are based on the fact that in the case of dilute solutions the difference between the freezing or boiling points of a solution and a solvent is proportional to the number of moles n of a solute. For example, the freezing point depression

$$\Delta T_f = E_s n \tag{16.1}$$

where E_s is the cryoscopic constant, i.e., the freezing point depression of the solvent when 1 mole of any substance is dissolved in 1000 g of it.

When studying low-molecular substances one usually uses solutions of concentration of approx. 1 g/100 ml of a solvent, which at $M \approx 100$ corresponds to a number of moles $n \approx 0.01$. If the cryoscopic constant $E_s = 5$, the quantity $\Delta T_f = 0.05\,^{\circ}C$. Such a difference of temperatures can be measured comparatively easily by conventional methods.

At the same concentration of a solution, if the molecular mass of a solute $M = 10^6$, the value of $n = 10^{-6}$. Hence, $\Delta T_f = 5 \times \times 10^{-6}$. No existing methods can sense such insignificant changes of temperature. For this reason, the cryoscopic and ebulliometric methods are useless for determining the molecular mass of high-molecular substances. The conventional cryoscopic method can be used to determine molecular mass up to 15 000. Precision ebulliometry enables determination of molecular masses up to 30 000.

The methods used in practice for determining the molecular mass and size of macromolecules in dilute solutions are discussed below.

16.1. METHODS OF DETERMINING MOLECULAR MASS

16.1.1. Osmometry

The dependence of the reduced osmotic pressure on concentration for dilute polymer solutions, expressed by Eq. (13.54) (see Chap. 13), is shown graphically in Fig. 16.1. In accordance with

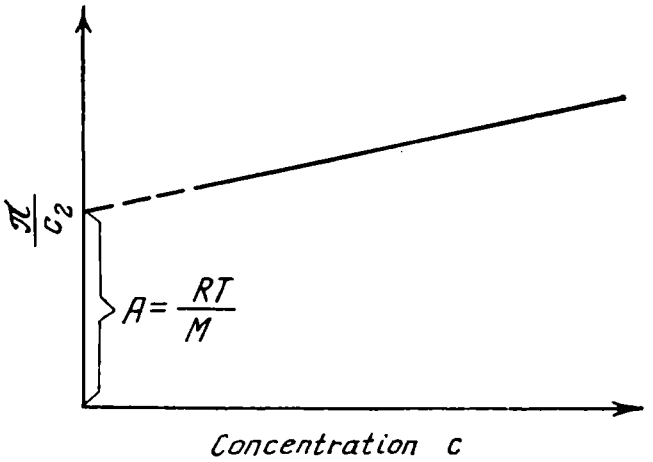

Fig. 16.1. Variation of reduced osmotic pressure with concentration

this equation the ordinate intercept of the graph is equal to the reduced osmotic pressure at infinite dilution:

$$RTA_1 = \lim_{c_2 \to 0} \frac{\pi}{c_2} \tag{16.2}$$

Assuming the laws of ideal solutions to be valid at infinite dilution, we may write

$$\pi = cRT \tag{16.3}$$

where $c = \frac{n}{V}$ = concentration of solution

n = number of moles of polymer

V = volume of solution, ml.

Since $n = m_2/M$ (where m_2 is the mass of a polymer and M is its molecular mass), the quantity π equals

$$\pi = \frac{m_2}{VM} RT \tag{16.4}$$

The quantity m_2/V is the concentration of a polymer in g/ml. Hence,

$$RTA_1 = \lim_{c_2 \to 0} \frac{\pi}{c_2} = \frac{RT}{M} \tag{16.5}$$

Solving Eqs. (16.5) and (16.2) simultaneously, we have

$$A_1 = \frac{1}{M} \tag{16.6}$$

Hence, the first Virial coefficient depends on the molecular mass of a polymer and can be calculated from the ordinate intercept of the line $\pi/c_2 = f(c_2)$.

Thus, to determine the molecular mass of a polymer it is necessary to measure the osmotic pressure of solutions at several concentrations and extrapolate the resulting line to zero concentration.

The instruments used for determining molecular mass by this method are called *osmometers*. The working principle of an osmometer is that the solvent, separated from the solution by a semipermeable membrane, passes through the latter into the solution until the level of the solution in a capillary stops rising.

In this case, the weight of the hydrostatic column of the solution is equal to osmotic pressure. However, the liquid in the capillary can rise partially owing to the presence of capillary forces. To take account of these forces, a capillary immersed in a solvent and having the radius of the osmometer capillary is put next to the latter. The difference of levels in the osmometer capillary and in a control capillary is the measure of osmotic pressure. Two methods, the static and the dynamic, are most commonly used.

The *static method* consists in measuring the equilibrium difference of levels in the osmometer. The *dynamic method* is based on measuring the rate of penetration of a solvent through the membrane, depending on the pressure applied.

Osmometers intended for measuring osmotic pressure by the static method are very simple in design, and that is their advantage over other types. But their common limitation is that attainment of equilibrium takes a long time. While equilibrium is being established, the concentration of the solution near the membrane may increase as a result of adsorption of polymer, which is not taken into account and leads to errors in determinations. However, this shortcoming is not of a fundamental nature and can be eliminated by proper production and storage of membranes.

The static method is usually not recommended for determining molecular mass of polymers capable of crosslinking.

The main advantage of the dynamic method is speed of measurement.

The reliability of osmometric measurements depends to a considerable extent on proper choice of membranes, which must be permeable to the solvent and impermeable to the polymeric solute. First of all, the membrane must not swell to any great extent in the solvent, and secondly, it should be sufficiently fine-porous to allow the solvent molecules to pass through freely.

At present membranes are prepared from cellophane and specially treated films of denitrated cellulose nitrate. The use of untreated cellophane involves great difficulties in connection with its small pore radius, as a result of which a long time is required to reach equilibrium. Treatment of the cellophane with an ammonia solution or other reagents increases the pore size very little. For this reason cellophane is usually used for measuring molecular masses of very low-molecular polymers. Membranes made of denitrated cellulose nitrate are much more satisfactory.

Before determining the molecular mass by the osmometric method the polymer should be thoroughly freed from impurities. This is usually done by reprecipitation. Working solutions of various concentrations, 0.5, 0.25, and 0.075 per cent, are prepared from a purified 1 per cent stock solution by dilution, leaving $^1/_5$ of the 1 per cent solution undiluted for exact determination of its concentration.

To calculate the molecular mass of a polymer the osmotic pressure values obtained for the different solutions are divided by the corresponding concentrations and the resulting reduced osmotic pressures are plotted in π/c_2 versus c_2 coordinates. The straight line obtained in this way is extrapolated to zero concentration (to its intersection with the ordinate axis) and the resulting value of $(\pi/c_2)_{c_2 \to 0} = A_1$ is substituted into Eq. (16.6) from which the molecular mass is calculated:

$$M = \frac{1}{A_1} = \frac{RT}{\left(\frac{\pi}{c_2}\right)_{c_2 \to 0}} \tag{16.7}$$

To express the osmotic pressure in atmospheres, the quantity π, expressed in centimetres of the solution column, should be multiplied by the density of a solvent, which is taken equal to the density of a dilute solution, and divided by the density of mercury and by 76. Since the solution concentration is in g/100 ml, the numerator should be multiplied by 10 to obtain the concentration of the solution referred to one litre. Then

$$M = \frac{0.082T \times 13.6 \times 76 \times 10}{d_1\left(\frac{\pi}{c_2}\right)_{c_2 \to 0}} \tag{16.8}$$

where T = temperature of an experiment, degrees K
d_1 = density of a solvent.

Determination of the molecular mass by osmometry is one of the most accurate methods. The experiment however is long and tedious, and cannot be used in practice for fast molecular mass determination.

Osmometry can be used for determining molecular masses from 10^4 to 10^6.

16.1.2. Light Scattering

It is known that media may be transparent or turbid. The turbidity of a medium is due to scattering of light. If the intensity of incident light is I_0, and on passage of the light through a medium of thickness x the incident intensity is reduced to I as a result of scattering (absorption of light by the medium is excluded), the turbidity of the medium is determined by the equation

$$\frac{I}{I_0} = e^{-\tau x} \tag{16.9}$$

Hence, turbidity characterizes the fraction of the primary light beam scattered in all directions on passage through some medium with thickness of 1 cm.

The scattering power of a substance is characterized by the coefficient of scattering R determined by the relation

$$R = \frac{I}{I_0} \cdot \frac{r^2}{v} \tag{16.10}$$

where I_0 and I = scattered and incident intensities
r = distance from scattering volume to observer
v = scattering volume.

For particles that are small compared to the wavelength of the incident light, turbidity is related to the light scattering coefficient by the equation

$$\tau = \frac{16}{3}\pi R_{90} \tag{16.11}$$

where R_{90} is the scattering coefficient at 90°.

It was thought at first that the medium scatters light owing to the presence in it of particles of a definite size (colloidal particles). Media free from such particles were termed *optically empty*. At present it is commonly known that no optically empty media exist. Any fluid (and even gases), no matter how pure, is capable of scattering light. Light scattering is caused by density and concentration fluctuations (if the medium is a solution), i.e., by deviation of the density and concentration from their uniform values. The clusters or associates formed serve as the centres of light scattering.

The total intensity of scattered light is the sum of the intensity due to fluctuation of density and the fluctuation of concentration:

$$I_{tot} = I' + I'' \tag{16.12}$$

In conformity with this,

$$R_\theta = R'_\theta + R''_\theta$$

whence

$$I'' = I - I'; \quad R''_\theta = R_\theta - R'_\theta$$

These quantities are known as excess intensity of light scattering and excess coefficient of light scattering, respectively.

On the basis of Smolukhovsky's ideas of density and concentration fluctuations, Einstein developed a theory of light scattering by liquids and solutions. According to this theory, concentration fluctuations always arise in the solution, resulting in light scattering. The scattered intensity I'' caused by concentration fluctuations for a nonpolarized ray is expressed by the following equation:

$$I'' = I_0 \frac{2\pi^2 v V_1^0 c_2 (n_0)^2}{N_A r^2 \lambda^4 \frac{d \ln f}{dc_2}} \left(\frac{\partial n}{\partial c_2}\right)^2 (1 + \cos^2\theta) \tag{16.13}$$

where I_0 = incident intensity
v = scattering volume
V_1^0 = molar volume of a solvent
c_2 = concentration of a solution
n_0 = refractive index of a solvent
$\partial n/\partial c_2$ = specific refractive increment
N_A = Avogadro's number
r = distance from scattering volume to the observer
λ = wavelength of incident light in vacuum
f = fugacity of a solvent
π = Piphagorian number.

Substitution into Eq. (16.13) of the value of R from Eq. (16.10) for excess scattering * at 90° yields

$$R''_{90} = \frac{2\pi^2}{N_A \lambda^4} \frac{V_1^0 c_2 (n_0)^2 \left(\frac{\partial n}{\partial c_2}\right)^2}{\frac{\partial \ln f}{\partial c_2}} \tag{16.14}$$

In 1944 Debye applied Einstein's theory to dilute polymer solutions. At very high dilutions ($c_2 < 0.5$ g/100 ml) the formation of associates is not very probable, and it is therefore assumed that the scattering centres are molecular coils, which are curled flexible

* Excess light scattering is caused only by concentration fluctuations.

macromolecules (Chap. 4). If the coil size is not greater than 400 Å, i.e., comes within the interval 0.05λ-0.1λ, Einstein's theory applies fully and Eq. (16.14) may be used. Expressing the fugacity through osmotic pressure (Chap. 13)

$$\frac{\partial \ln f}{\partial c_2} = -\frac{V_1^0}{RT}\frac{\partial \pi}{\partial c_2}$$

and representing the quantity π as a series with Virial coefficients

$$\frac{\pi}{RT} = A_1 c_2 + A_2 c_2^2$$

we get the following expression for determining the turbidity of a polymer solution:

$$R''_{90} = \frac{2\pi^2 (n_0)^2 \left(\frac{\partial n}{\partial c_2}\right)^2}{3N_A \lambda^4} \cdot \frac{c_2}{\frac{1}{M} + 2A_2 c_2} \qquad (16.15)$$

where A_2 = second Virial coefficient
M = molecular mass of a polymer
π = Piphagorian number.

Whence

$$\frac{Kc_2}{R''_{90}} = \frac{1}{M} + 2A_2 c_2 \qquad (16.16)$$

where

$$K = \frac{2\pi^2 (n_0)^2 \left(\frac{\partial n}{\partial c_2}\right)^2}{\lambda^4 N_A} \qquad (16.17)$$

or

$$\frac{Hc_2}{\tau} = \frac{1}{M} + 2A_2 c_2 \qquad (16.18)$$

where

$$H = 32\pi^3 (n_0)^2 \left(\frac{\partial n}{\partial c_2}\right)^2 / 3N_A \lambda^4 \qquad (16.19)$$

According to Eqs. (16.16) amd (16.18), the dependence $\frac{Kc_2}{R''_{90}}$ or $\frac{Hc_2}{\tau}$ on c_2 is expressed by straight lines, whose slope can be used to calculate the second Virial coefficient. The segment cut off by these lines on the ordinate is equal to $\frac{1}{M}$.

Thus, in order to determine the molecular mass of a polymer by this method, it is necessary to determine, by means of a refractometer or an interferometer, the refraction index of a solvent and its change with concentration *dn/dc* (increment of the refraction

index) and, by means of a nephelometer, excess light scattering R''_{90}.

Eqs. (16.16) and (16.18) are valid for determining the molecular mass of comparatively low-molecular polymers. When the values of the molecular mass are high, the size of a coil is considerably larger than 0.05λ-0.1λ. Therefore, the particle regions which are apart from one another scatter light with some phase difference; this difference is greater, the greater is the angle θ (Fig. 16.2). As a result of internal interference, the intensity of

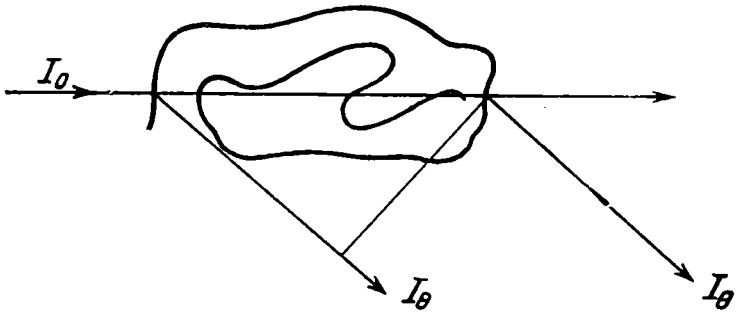

Fig. 16.2. Scattering of light by large particles

light scattering diminishes for all angles except $\theta = 0$. This is taken into account either by making a correction for internal interference in the equation (Debye's method) or by extrapolating the quantities obtained to the angle $\theta = 0$ (Zimm's method).

Debye's Method. Debye gave a solution for the factor of internal interference $P(\theta)$ for the scattering particles of different shape.

For spheres:

$$P(\theta) = \left[\frac{3}{x^3}(\sin x - x\cos x)\right]^2 \qquad (16.20)$$

where

$$x = \frac{\pi}{\lambda} 2 \sin\frac{\theta}{2} L$$

For rods:

$$P(\theta) = \frac{1}{x}\int_0^{2x} \frac{\sin\theta}{\theta}\, d\theta - \left(\frac{\sin x}{x}\right)^2 \qquad (16.21)$$

where

$$x = \left(2\pi\frac{L}{\lambda}\right)\sin\frac{\theta}{2}$$

For Gaussian coils (p. 102):

$$P(\theta) = \frac{2}{y}(e^{-y} - 1 + y) \qquad (16.22)$$

where

$$y = \frac{2\pi^2 \bar{h}^2}{3\lambda^2} \sin^2 \frac{\theta}{2}$$

where L = radius of the sphere or length of the rod

$(\bar{h}^2)$ = root-mean-square end-to-end distance of a chain (p. 102).

Since macromolecules mostly assume the shape of coils in dilute solutions, formula (16.22) is used very often; this formula makes it possible to calculate also the root-mean-square end-to-end distance of a macromolecule, i.e., to estimate its dimensions.

To calculate the value of θ, measurement is taken of the intensity of light scattering at two angles, which are complimentary relative to one another and symmetrical with respect to 90° (usually at angles of 45° and 135°). Their ratio is equal to the ratio of corrections and is known as the *asymmetry coefficient*

$$Z = \left(\frac{R''_{45}}{R''_{135}}\right) = \left(\frac{P_{45}}{P_{135}}\right) \quad (16.23)$$

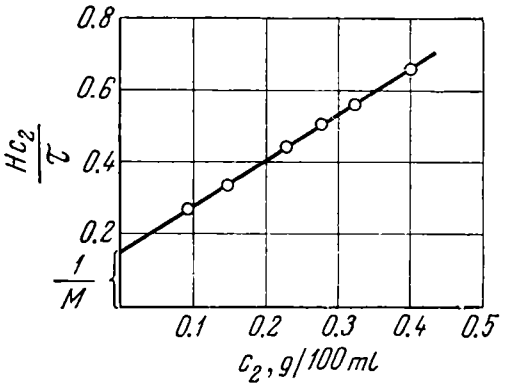

Fig. 16.3. Dependence of Hc_2/τ on concentration of solution

The quantity Z depends on the concentration of a solution. To obtain a value which is independent of concentration, the quantity $\frac{1}{Z-1}$ is extrapolated to infinite dilution and the characteristic value $[Z]$ is obtained. When $[Z]$ is known, the value of $P(\theta)$ is found from the existing tables.

The equation for determining the molecular mass of a polymer assumes the form

$$\frac{Kc_2}{R''_{90}} = \frac{Hc_2}{\tau} = \frac{1}{M \cdot P(\theta)} + 2A_2 \cdot c_2 \quad (16.24)$$

Hence, the experiment consists in the measurement of: (1) the excess light scattering of solutions of several concentrations in the concentration range of 1 g/100 ml at three angles, and (2) the increment of the refraction index.

Then, a graph is plotted in the coordinates $\frac{Hc_2}{\tau}$ vs. c_2. In conformity with Eq. (16.24), a straight line is obtained that is extrapolated to zero concentration. The value of $\frac{1}{M}$ is calculated by

the segment intersected on the ordinate, and the second Virial coefficient, A_2, by the slope of this line (Fig. 16.3).

Zimm's Method. In this method, double extrapolation is performed: to zero concentration and to the zero value of the angle ϑ. Measurement is taken of R''_θ for solutions of several concentrations at different angles in the range of usually 30°-150°, and the graph of dependence of $\frac{Kc_2}{R''_\theta}$ on concentration is plotted for various angles of θ. In this case, the concentration values are multiplied by the constant K, which should be such that Kc_{max} would be several units (K = 1000-5000). The dependence $\frac{Kc_2}{R''_\theta} = f(c_2)$ is expressed by parallel lines (steeper lines in Fig. 16.4). They are all extrapolated to zero concentration. Slanter lines represent the graph of dependence of $\frac{Kc_2}{R''_\theta}$ on $\sin^2\frac{\theta}{2}$ at different given concentrations. Each line is extrapolated to the zero angle. The extreme left line is a totality of points which correspond to $\sin^2\frac{\theta}{2}=0$, while the lower line corresponds to zero concentration for all angles. Both lines ($\theta = 0$ and $c = 0$) intersect on the ordinate at one point, which corresponds to $\frac{1}{M}$.

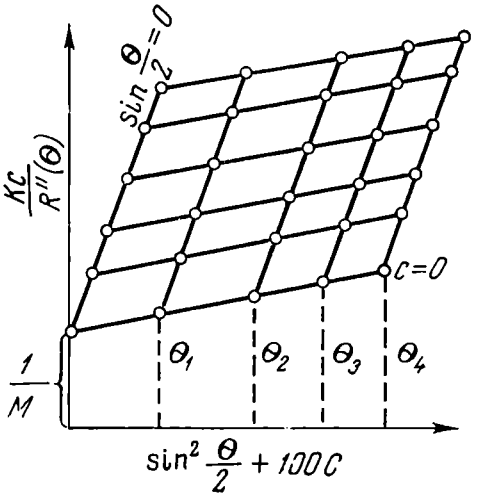

Fig. 16.4. Zimm diagramm

This method is more precise and makes it possible to calculate the values of molecular masses of polymers without assumption of the shape of macromolecules in a solution.

16.1.3. Viscometry

The first to draw attention to the relationship between the viscosity of dilute solutions of polymers and their molecular mass was Staudinger, who established the following empirical dependence:

$$\eta_{sp} = KMc \qquad (16.25)$$

where η_{sp} = specific viscosity of a solution
K = constant
M = molecular mass of a dissolved polymer
c = concentration of a polymer in a solution.

To calculate the molecular mass from Eq. (16.25) it is necessary to determine the specific viscosity of a solution of given concentration c and the constant K. In his work Staudinger employed solutions of concentration approx. 0.25 g/100 ml; the constant K was calculated from the molecular mass of low-molecular members of the polymer-homologous series, determined cryoscopically:

$$K = \frac{\eta_{sp}}{M_{cr}c} \tag{16.26}$$

Obviously, this method of determining the coefficient K is based on the assumption of its independence of molecular mass within a polymer-homologous series.

But Eq. (16.26), which was used for determining molecular mass, proved inaccurate.

First of all, the coefficient K is not a constant value, but depends on the molecular mass of a polymer. Thus, for polystyrene with a molecular mass of 438 $K = 7 \times 10^{-4}$, while for polystyrene with a molecular mass of 193 000 it is 1.25×10^{-4}. Hence, the value of K determined for solutions of lower polymer homologues cannot be substituted into Eq. (16.25) for calculating the molecular mass of high polymers.

Secondly, Staudinger's equation reflects the concentration dependence of specific viscosity incorrectly. According to this equation, $\eta_{sp}/c = KM$, i.e., the reduced viscosity is independent of concentration. But experimental data show that the η_{sp}/c vs. c dependence is represented graphically by a straight line with a definite slope (p. 456). Evidently it would be more correct to relate the molecular mass of a polymer not to the specific viscosity, but to a viscosity value that is independent of the solution concentration, i.e., to the intrinsic viscosity. For this reason the following empirical relation has become very popular:

$$[\eta] = KM^a \tag{16.27}$$

where $[\eta]$ = intrinsic viscosity of a solution
M = molecular mass of a dissolved polymer
K and a = constants characterizing given polymer-solvent system.

Intrinsic viscosity is determined from the relative viscosity of dissolved polymer solutions (p. 455). Knowing this quantity the specific and reduced viscosities are calculated and a plot of η_{sp}/c vs. c is made. The value of $[\eta]$ is determined by extrapolation of the resulting line to zero concentration. The values of K and a are found as follows. Several fractions of the same polymer are obtained and their molecular masses (M', M'', M''', etc.) are determined osmometrically or by light scattering (p. 493). Then the

intrinsic viscosities $[\eta]'$, $[\eta]''$, $[\eta]'''$, etc., of these fractions are found by the method described above.

From Eq. (16.27) we have

$$\log [\eta] = \log K + a \log M \tag{16.28}$$

Hence, $\log [\eta]$ vs. $\log M$ is represented by a straight line of slope a (Fig. 16.5). The intercept of this line on the viscosity axis is numerically equal to $\log K$. Hence, the values of K and a can be determined graphically. These values for numerous polymer-solvent systems are given in Tables 16.1 and 16.2. It must be borne in mind that viscosities should be determined by using the same solvent as that for which constants K and a were found.

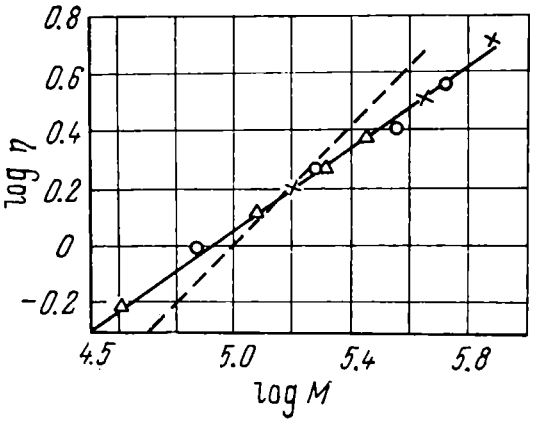

Fig. 16.5. Log $[\eta]$ vs. log M for a benzene solution of polybutadiene rubbers. (The dashed line has been calculated from Standinger's equation.)

The viscometric method of determining molecular mass is very convenient owing to the simplicity of the equipment used. This method can be employed in any plant or shop laboratory, but the resulting absolute values of molecular mass of a polymer are not always sufficiently accurate. This is due to the fact that the viscosity of a dilute solution is a function of molecular size and molecular size is not the same as molecular mass. With the same molecular mass a molecule may be linear or branched, i.e., it may have different sizes and shapes, which affects the intrinsic viscosity value differently. If the constants K and a are determined for a less branched polymer and then employed for studying a more branched polymer of the same chemical composition, or vice versa, the molecular masses calculated from Eq. (16.27) may prove incorrect. That is why the viscometric method can be recommended not for determining absolute molecular masses but only changes in molecular mass during various processes (polymerization, degradation, etc.).

16.1.4. Diffusion

Diffusion is directed thermal motion of molecules or very fine particles, and it always occurs from the place where there are many of them to the place where there are few of them. Consequently, the concentration in a system becomes uniform as a

result of diffusion. The diffusion rate or the amount of the diffusing substance per unit time, dQ/dt, depends on the concentration gradient, i.e., on a change in concentration with the distance $-dc/dx$. This relation is expressed by Fick's first law:

$$\frac{dQ}{dt} = -D\frac{dc}{dx}S \tag{16.29}$$

where S = cross-sectional area through which a substance diffuses.

The proportionality factor D is known as the diffusion coefficient.

If $S = 1$ cm^2, $t = 1$ s, and $dc/dx = 1$, then $D = Q$. This means that the coefficient of diffusion is numerically equal to the amount of substance diffusing through unit cross-sectional area in 1 s at a gradient of concentration of unity. The dimensionality of the coefficient of diffusion can be derived from Eq. (16.29):

$$[D] = \left[\frac{Q}{\frac{dc}{dx}St}\right] = \frac{\text{g} \cdot \text{cm}^3 \cdot \text{cm}}{\text{g} \cdot \text{cm}^2 \cdot \text{s}} = \frac{\text{cm}^2}{\text{s}}$$

Diffusion is directly connected with molecular mobility; consequently, its rate should depend on their dimensions. Borshchov was first to draw attention to this. The quantitative relationship between the coefficient of diffusion D and the size of a diffusion particle was obtained theoretically by Einstein:

$$D = \frac{RT}{6\pi\eta r N_A} \tag{16.30}$$

where η = viscosity coefficient of the medium in which diffusion is occurring
r = radius of diffusing particle
N_A = Avogadro's number.

Equation (16.30) is valid for diffusing colloidal particles and for molecules. If the molecule is sphere-shaped, its volume $V = 4/3\,\pi r^3$. Multiplying this quantity by the density d, we get the mass of the molecule, and multiplying further by Avogadro's number N_A, we get molecular mass, i.e.,

$$\frac{4}{3}\pi r^3 N_A d = M$$

Hence

$$r^3 = \frac{3M}{4\pi N_A d} \tag{16.31}$$

Substituting Eq. (16.30) in Eq. (16.31), we obtain an expression for the molecular mass of the spherical molecule:

$$M = \frac{R^3 T^3 d}{162\pi^2 \eta^3 N_A^2 D^3} \tag{16.32}$$

If the molecule is not spherical, a correction is made on the basis of the fact that the ratio of the diffusion coefficients of spherical and non-spherical particles which move at the same velocity is equal to that of internal friction forces:

$$\frac{D_{nsph}}{D_{sph}} = \frac{f_{sph}}{f_{nsph}} \tag{16.33}$$

The ratio $\frac{f_{nsp}}{f_{sph}}$ is known as *asymmetry factor*. It is calculated for particles of different shape.

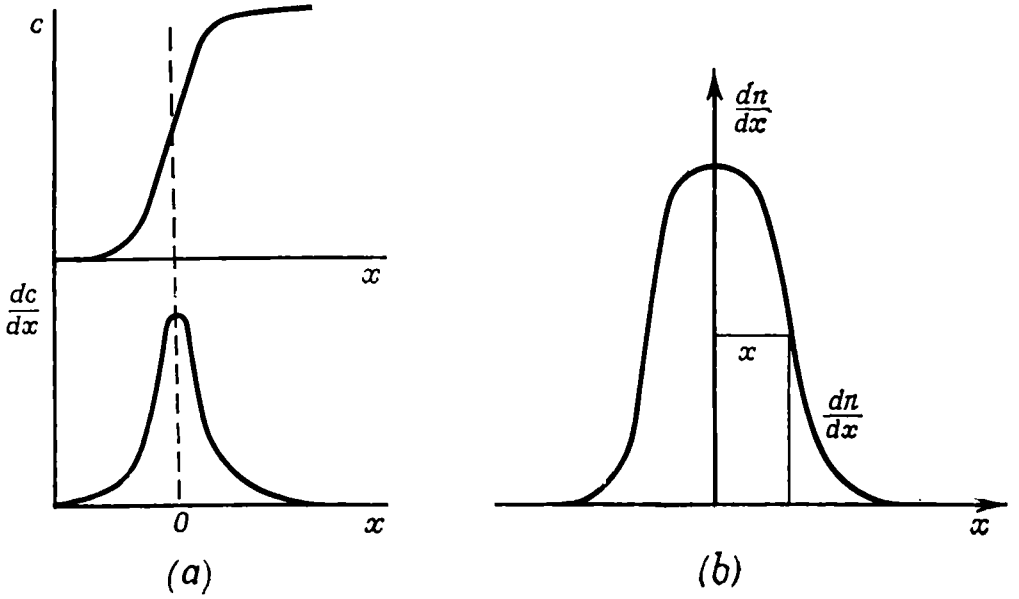

Fig. 16.6. Curves of distribution of concentration, concentration gradient (*a*) and refractive index gradient (*b*)

However, all the existing equations are invalid for the diffusion of macromolecules, and at present there is no equation which connects the coefficient of translational diffusion of macromolecules with their molecular mass. Therefore, the molecular mass is calculated by empiric relationships, which are established in the following way.

The coefficient of translational diffusion of macromolecules is determined, as usual, by using Fick's second law:

$$\frac{dc}{dt} = -D\frac{d^2c}{dx^2} \tag{16.34}$$

The methods of determining the diffusion coefficient are based on the measurement of the rate at which the boundary between the solution of the polymer under consideration and the solvent is blurred. The distribution of concentration and of the gradient

of concentration dc/dx near the boundary at different times of observation is expressed by the curves given in Fig. 16.6 (*a*, *b*). The distribution of dc/dx has the form of a Gaussian curve with the maximum on the boundary between the solution and the solvent ($x = 0$). It is described by Wiener's equation, which is obtained by integrating Eq. (16.34) at definite allowances:

$$\frac{dc}{dx} = \frac{c_0}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}} \tag{16.35}$$

where c_0 = concentration of the solution in g/cm^3
t = time from the beginning of diffusion in seconds
x = distance of the gradient under consideration from the boundary.

To register the experimental results, optical methods are usually used; for example, the refraction index n of a solution and its gradient dn/dx along the diffusion direction are determined. For concentrations at which measurement is being taken ($\sim$0.5 g/ml), the gradient of the refraction index is directly proportional to the gradient of concentration:

$$\frac{dn}{dx} = \text{const}\,\frac{dc}{dx} \tag{16.36}$$

and

$$c_0 = n_1 - n_0 \tag{16.37}$$

where n_0 and n_1 = refraction indices of the solvent and the solution, respectively.

Then, Eq. (16.35) will assume the form

$$\frac{dn}{dx} = \frac{n_1 - n_0}{\sqrt{4\pi Dt}} e^{-\frac{x^2}{4Dt}} \tag{16.38}$$

In this case, the distribution of the gradient of the refraction index is also expressed by the Gaussian curve (Fig. 16.6*b*).

The simplest method of calculation is the *method of the maximum ordinate*, which apparently corresponds to $x = 0$. In this case, the term $e^{-x^2/4Dt}$ in Eq. (16.38) becomes zero and the equation is simplified:

$$\left(\frac{dn}{dx}\right)_{\max} = \frac{n_1 - n_2}{\sqrt{4\pi Dt}} \tag{16.39}$$

The area under the curve can be determined by the equation

$$A = \int \left(\frac{dn}{dx}\right) dx = \int_{n_0}^{n_1} dn = n_1 - n_0 \tag{16.40}$$

Consequently,

$$\left(\frac{dn}{dx}\right)_{\max} = \frac{A}{\sqrt{4\pi Dt}} \tag{16.41}$$

or

$$D = \frac{A^2}{4\pi t \left(\frac{dn}{dx}\right)^2_{max}} \tag{16.42}$$

The quantity D thus obtained turns out to be dependent on concentration. Therefore, the concentration dependence of D is studied, and the value of D_0 is obtained when extrapolating to zero concentration.

Tsvetkov's polarization diffusiometer makes it possible to take measurements for solutions whose concentration is several thou-

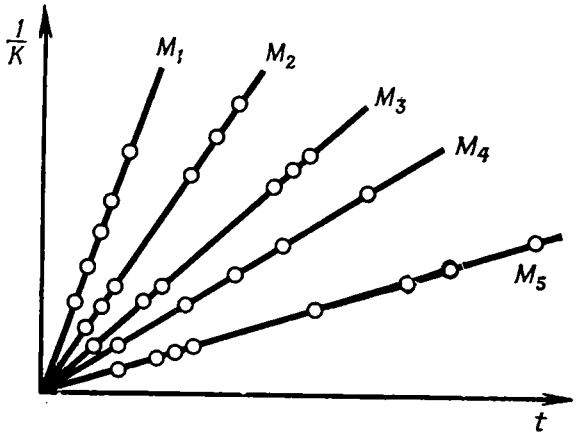

Fig. 16.7. Time dependence of $\frac{1}{K}$ for different polymer fractions ($M_1 < M_2 < M_3 < M_4 < M_5$)

sandths of a per cent. With this device, measurement is taken only at one concentration even for polymers of a very great molecular mass.

If we denote $\frac{A^2}{2\pi (dn/dx)^2_{max}}$ by σ^2, while $2\sigma^2 = \frac{1}{K}$, Eq. (16.42) will assume the form

$$\frac{1}{K} = D_0 t \tag{16.43}$$

Consequently, the dependence of $\frac{1}{K}$ on t is expressed by a straight line which passes through the coordinate origin. Its slope is equal to the diffusion coefficient. A typical graph of such a dependence for polymer fractions of different molecular masses is given in Fig. 16.7.

Experiments show that for very many polymers in a wide range of molecular masses, the dependence of the diffusion coefficient

on the molecular mass can be expressed by the equation

$$D_0 = K_D M^{-b} \tag{16.44}$$

where K_D = constant for the given polymer-solvent system
b = parameter.

16.1.5. Ultracentrifugation

It is common knowledge that the size of particles can be determined by the rate of their sedimentation. A sedimenting particle is under the influence of two forces, namely, the force of the gravity field and the resistance of the medium, i.e., the force of internal friction. If the particle is spherical in shape, according to Stokes' law its internal friction equals $6\pi\eta ru$. If these two forces are equal, the particle will be sedimented at a constant rate:

$$\frac{4}{3}\pi r^3 (d_к - d_0) g = 6\pi\eta ru \tag{16.45}$$

where r = particle radius
d_k = particle density
d_0 = density of medium
g = gravity acceleration
η = viscosity of medium
u = rate of sedimentation of the particle.

The values of r and u can be determined from Eq. (16.45):

$$r = \sqrt{\frac{9u\eta}{2g(d_к - d_0)}} \tag{16.46}$$

and

$$u = \frac{2}{9} \cdot \frac{r^2}{\eta} g (d_к - d_0) \tag{16.47}$$

It follows from Eq. (16.46) that to determine the radius of a particle it is necessary to measure the rate of its sedimentation, i.e., the path S it traverses in a definite length of time.

However, very small particles sink at low rates. For example, the time of sedimentation (the reciprocal of the rate of sedimentation) of a particle of radius $r = 10^{-7}$ mm with $d_k \approx 2.5$ g/cm^3 is approximately 100 years.

In 1912 A. Dumansky suggested using a centrifugal field to speed up sedimentation, and in 1923 Svedberg invented the ultracentrifuge, an apparatus in which accelerations are created, exceeding the acceleration due to gravity by hundreds of thousands of times.

Sedimentation of molecules in the centrifugal field occurs in a direction perpendicular to the axis of rotation. A molecule of volume v is gradually sedimented by the centrifugal force. During

sedimentation its distance from the axis of rotation (x) keeps changing all the time. The centrifugal force equals the product of the particle mass by the acceleration of the centrifugal field $\omega^2 x$, where ω is the angular velocity of rotation. The force of resistance is expressed by Stokes' law. For spherical particles

$$v(d_k - d_0)\omega^2 x = 6\pi\eta r \frac{dx}{d\tau}$$

or

$$vd_k\left(1 - \frac{d_0}{d_k}\right)\omega^2 x = 6\pi\eta r \frac{dx}{d\tau} \qquad (16.48)$$

where r = radius of a sedimenting spherical molecule
$dx/d\tau$ = rate of sedimentation.

If one mole of substance is sedimenting, then $vd_kN_A = M$. Thus,

$$M\left(1 - \frac{d_0}{d_k}\right)\omega^2 x = 6\pi\eta r N_A \frac{dx}{d\tau} \qquad (16.49)$$

From Eq. (16.30) it follows that

$$6\pi\eta r N_A = \frac{RT}{D}$$

where D = diffusion coefficient
R = gas constant
T = absolute temperature.

Therefore

$$M\left(1 - \frac{d_0}{d_k}\right)\omega^2 x = \frac{RT}{D} \cdot \frac{dx}{d\tau} \qquad (16.50)$$

Hence,

$$M = \frac{RT}{D(1 - \bar{v}_2 d_0)} \cdot \frac{dx/d\tau}{\omega^2 x}$$

where $\bar{v}_2 \cong \frac{1}{d_k}$ = partial specific volume of a polymer in solution.

The relation $\frac{dx/d\tau}{\omega^2 x}$ is known as the *sedimentation coefficient* S. Its value, like the diffusion coefficient, depends on concentration. Therefore, both of them must be extrapolated to infinite dilution. The value of S, extrapolated to infinite dilution, is known as *sedimentation constant* S_0. Then, the final equation will assume the form

$$M = \frac{RTS_0}{D_0(1 - \bar{v}_2 d_0)} \qquad (16.51)$$

According to Eq. (16.51), to calculate the molecular mass of a polymer it is necessary to know the diffusion coefficient and the sedimentation constant.

The coefficient of diffusion is determined as was shown on p. 501. The sedimentation constant is determined by means of an

ultracentrifuge. For this purpose, a beam of light is passed through a cell containing a solution of the polymer, placed in an ultracentrifuge. The light beam falls on a photographic plate situated beyond the cell. When the cell is rotated, the interface

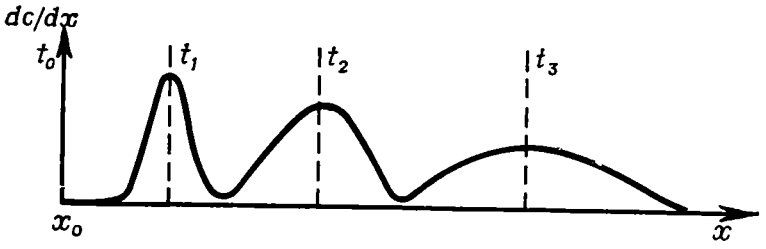

Fig. 16.8. Variation of concentration gradient during centrifugation

between the solution and the solvent shifts gradually as the substance is sedimented, and the light is absorbed to a different extent at different heights of the cell. The plate shows bands of different optical densities. The rate of sedimentation can be determined by

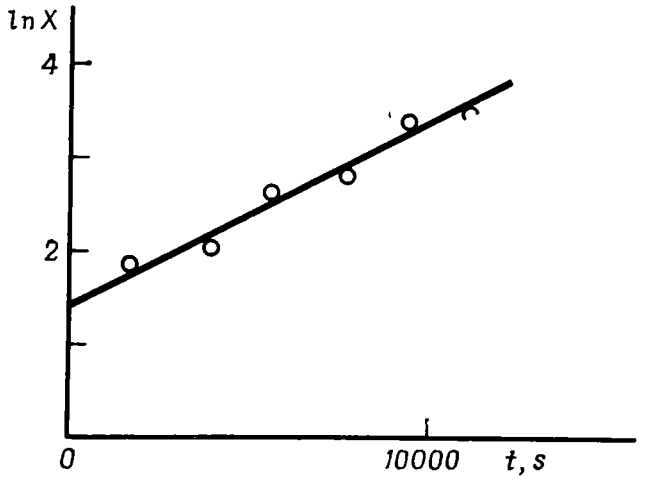

Fig. 16.9. Graph of time dependence of $\ln x$

photometrically measuring exposures made at definite time intervals as was shown on page 506. In this case, the so-called sedimentation curve may be obtained, i.e., the curve of distribution of the concentration gradient along the height of a cell at different times. For a monomolecular polymer, these curves are of the form given in Fig. 16.8. Since

$$S \equiv \frac{dx/dt}{\omega^2 x} = \frac{d \ln x}{\omega^2 dt} \tag{16.52}$$

the dependence of $\ln x$ on t should be expressed by a line, whose slope can be used to calculate the sedimentation coefficient S (Fig. 16.9). The value of x is determined from the position of the

maximum of the sedimentation curve. To preclude concentration effects of the quantity S, extrapolation is made to infinite dilution. In the region of sufficiently great dilutions, S changes with concentration according to the law

$$\frac{1}{S} = \frac{1}{S_0}(1 + Kc) \tag{16.53}$$

Hence, in order to calculate the sedimentation constant, $\frac{1}{S} = f(c)$ is plotted.

If the quantities S_0 and D_0 are known, the molecular mass of a polymer is calculated by Eq. (16.51). In addition, use is made of the equation

$$S_0 = K_s M^{(1-b)} \tag{16.54}$$

where K_s = constant for the given polymer-solvent pair
b = parameter entering Eq. (16.44).

The values of K_s and b for some polymer-solvent systems are given in literature. These equations can be used for calculating the molecular mass of a polymer by the experimentally determined values of constant sedimentation. The method of sedimentation in the ultracentrifuge is an absolute method for measuring the molecular mass of a polymer, since no assumptions on macromolecular conformations are made in it.

16.2. DETERMINATION OF MOLECULAR-MASS DISTRIBUTION OF POLIMERS

16.2.1. Distribution Curves

The difficulty of determining the molecular mass of polymers is due to the polydispersity of the latter, each sample containing molecules of different sizes. Therefore molecular masses, no matter by what method they are determined, are averages having different numerical values depending on the method by which they are measured. Calculation of various molecular mass averages is illustrated below.

Suppose we have

N_1 molecules of molecular mass M_1
N_2 molecules of molecular mass M_2
N_3 molecules of molecular mass M_3.

Usually two methods of calculating molecular mass averages of polymers are used:

(a) calculation of the arithmetical mean or number-average molecular mass $\bar{M}_n$;

(b) calculation of the weight-average molecular mass $\bar{M}_w$.

To calculate the *number-average molecular mass* $\overline{M}_n$ each molecular mass value is multiplied by the number of molecules having that value and the resulting products are added up, giving the sum of molecular masses of all the molecules; then this sum is divided by the total number of molecules:

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \dots}{\sum N_i} = \frac{\sum N_iM_i}{\sum N_i} \qquad (16.55)$$

To calculate the weight-average molecular mass $\overline{M}_w$ it is necessary to know the contribution of each given molecular mass to the total molecular mass. The total molecular mass equals $\sum N_iM_i$, and hence, the contribution of each molecular mass x_i equals

$$x_i = \frac{N_iM_i}{\sum N_iM_i} \qquad (16.56)$$

If each molecular mass is multiplied by its contribution to the total molecular mass and these products are added up, the resulting value is known as the *weight-average molecular mass*:

$$M_1x_1 + M_2x_2 + M_3x_3 + \dots = \overline{M}_w$$

or

$$\overline{M}_w = \frac{M_1N_1M_1}{\sum N_iM_i} + \frac{M_2N_2M_2}{\sum N_iM_i} + \frac{M_3N_3M_3}{\sum N_iM_i} + \dots$$

or

$$\overline{M}_w = \frac{\sum N_iM_i^2}{\sum N_iM_i} \qquad (16.57)$$

Now let us consider concrete examples of calculating average molecular mass values.

Suppose there are 100 polymer molecules of molecular mass 10^3, 200 molecules of molecular mass 10^4, and 200 molecules of molecular mass 10^5. Then

$$\overline{M}_n = \frac{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5}{100 + 200 + 200} = \frac{10^5\,(1 + 20 + 200)}{500} \cong$$

$$\cong 4.4 \times 10^4 = 44\,000$$

$$\overline{M}_w = \frac{100 \times 10^6 + 200 \times 10^8 + 200 \times 10^{10}}{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5} =$$

$$= \frac{10^8\,(1 + 200 + 20\,000)}{10^5\,(1 + 20 + 200)} = \frac{10^3 \times 20\,201}{221} \cong 91\,000$$

It is evident from this example that the number-average molecular mass of a polydisperse polymer does not coincide with its weight-average value, and that $\overline{M}_w$ is always greater than $\overline{M}_n$.

In monodisperse system $\bar{M}_w = \bar{M}_n$; the ratio $\bar{M}_w/\bar{M}_n$ is a measure of polydispersity. The value of $\bar{M}_w$ is very sensitive to the presence of molecules of higher molecular mass, and $\bar{M}_n$, of molecules of lower molecular mass.

Determination of the molecular mass of an unfractionated polydisperse polymer sample by different methods results in different numerical values of average molecular mass.

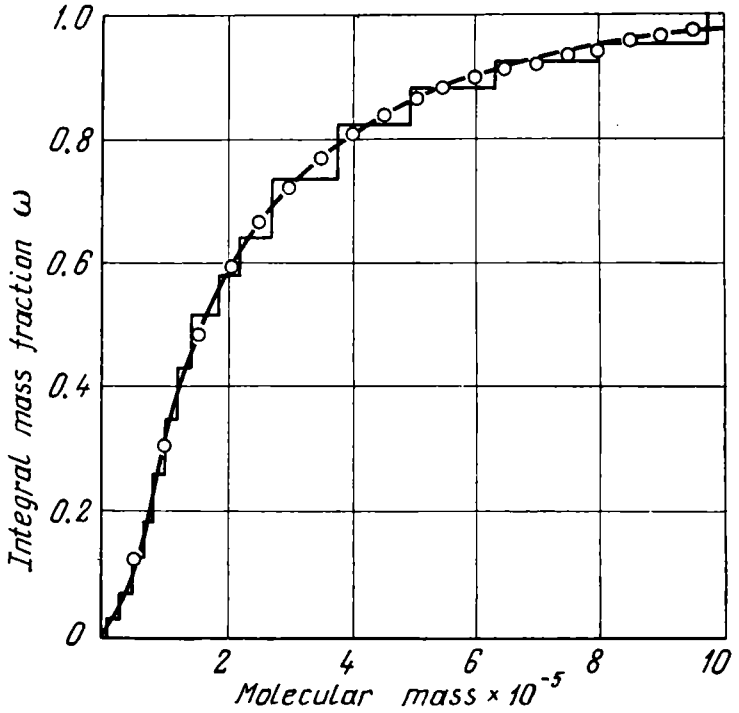

Fig. 16.10. Integral molecular-mass distribution curves of a polymer

Osmometry gives the number-average molecular mass, because of the dependence of the osmotic pressure on concentration, i.e., number of molecules. Light scattering yields weight-average values. Molecular masses determined by ultracentrifugation and diffusion are close to weight-average values. Measurement of intrinsic viscosities leads to the so-called *viscosity-average* or *average viscometric molecular mass*, which can be calculated from the equation

$$\bar{M}_v = \left[\frac{\sum N_i M^{1+a}}{\sum N_i M_i}\right]^{1/a} \qquad (16.58)$$

where a is the exponent in the equation $[\eta] = KM^a$.

In practice, $\bar{M}_v$ deviates from $\bar{M}_w$ by not more than 20 per cent. When $a = 1$, $\bar{M}_v = \bar{M}_w$.

Thus, determination of the molecular mass of unfractionated samples by different methods results in inherently different average

values. The molecular masses of samples with a wide molecular-mass distribution may differ by a factor of more than two. Only in the case of monodisperse polymers are the molecular masses determined by different methods likely to coincide.

By fractionating a polymer and determining the molecular and conventional masses of each fraction, what is known as the *integral molecular-mass distribution curve* can be plotted, marking the molecular masses of the fractions along the abscissa axis and the integral mass contribution of the fraction, i.e., the contribution of all fractions having molecular masses up to any given value — along the ordinate axis (Fig. 16.10).

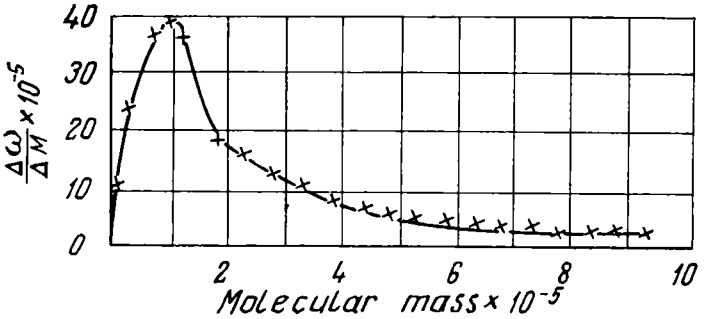

Fig. 16.11. Differential molecular-mass distribution curve of a polymer

Differentiation of the integral curve gives the *differential distribution curve*. This is done by marking points on the integral curve at definite molecular mass intervals and measuring the ordinate differences between each two neighbouring points. Each difference $\Delta\omega$ is then divided by the size of the interval ΔM. Then the resulting $\Delta\omega/\Delta M$ values are plotted against the average molecular masses for each interval (Fig. 16.11). The basic characteristics of a differential curve are the position of its peak and its width. The wider the curve, the wider the molecular-mass distribution.

The curve of the molecular-mass distribution of a polymer can be obtained directly from the data on sedimentation of a polymolecular polymer in the ultracentrifuge. Since every fraction settles at its own rate, the interface is very diffuse, and the sedimentation curve is considerably wider than for the monomolecular polymer. By using several equations, a transition is made from the gradient curves (Fig. 16.11) obtained by the method of rapid sedimentation to the molecular-mass distribution curves.

16.3. DETERMINATION OF DIMENSIONS OF MACROMOLECULES

The dimensions of macromolecules, as we have seen (p. 436), are estimated by the root-mean-square end-to-end distance, which

can be determined by data on the light scattering of dilute solutions or by their viscosity.

Light-Scattering Method. The quantity $(\bar{h}^2)^{1/2}$ is connected by a complicated equation with characteristic anisotropy [Z] (p. 497). The solution of this equation was given by Doty and Steiner. In their tables, they give values of $(\bar{h}^2)^{1/2}$ for various values of [Z]. By means of these tables, the experimenter plots a working graph of dependence of $(\bar{h}^2)^{1/2}$ on [Z], which is used to find the corresponding value of $(\bar{h}_2)^{1/2}$ on the basis of the value of [Z] determined experimentally.

Knowing this quantity for macromolecules, which act as Gaussian coils, one may calculate the radius of gyration

$$\bar{R}^2 = \frac{1}{6}\bar{h}^2 \tag{16.59}$$

Zimm's method makes it possible to calculate $\bar{R}^2$ directly from a diagram given in Fig. 16.4. For this purpose, the slope of the curve $\left|\frac{Kc}{R''_\theta}\right|_{\substack{c=0\\ \theta=0}}$ is determined, and its value of S_0 is substituted in the equation

$$\frac{S_0}{A_1} = \frac{1}{3}\bar{R}^2\frac{16\pi^2}{\lambda^2} \tag{16.60}$$

where λ = wavelength of incident light

$$A_1 = \frac{1}{M}.$$

For Gaussian coils, these data can be used to calculate $\bar{h}^2$ by the equation

$$\frac{\bar{h}^2}{\lambda^2} = \frac{9}{8\pi^2}\frac{S_0}{A_1} \tag{16.61}$$

The coil size thus determined depends on the solvent: the better the solvent thermodynamically, i.e., the better its quality (p. 389), the more does the coil swell and the greater are $(\bar{h}^2)^{1/2}$ and $\bar{R}^2$. To obtain information on the dimensions of a coil which is unperturbed by the solvent, measurement is taken in the θ-solvent (p. 437) and the values obtained have the subscript, $(\bar{h}^2_\theta)^{1/2}$ and $\bar{R}^2_\theta$.

The quantity $(\bar{h}^2)^{1/2}$ is determined **viscosimetrically** by the equation

$$[\eta] = \Phi_0\frac{(\bar{h}^2_0)^{3/2}}{M} \tag{16.62}$$

which was considered when the effect of the quality of a solvent on intrinsic viscosity was being discussed (p. 463).

It should be noted that the values of $(\bar{h}^2_\theta)^{1/2}$, calculated by Eq. (16.62) and determined from data on light scattering for the

same polymer in a solvent, do not always coincide. In addition, data on the dimensions of macromolecules that were obtained when the properties of dilute solutions in various θ-solvents were being studied do not coincide.

Indeed, the methods described on page 463 can be used to select several θ-solvents for which $A_2 = 0$ for one polymer. Theoretically, the coil should have unperturbed dimensions in solutions with all solvents, i.e., the exponent in the Mark-Kuhn-Houwink equation should be 0.5 (p. 460). However, these two conditions are not always observed, especially when a binary mixture of liquids is taken as the θ-solvent. This was shown by Benoit and Dondos. The table below gives some of their data.

TABLE 16.1. *Values of the Second Virial Coefficient A_2 and the Exponent a in the Equation $[\eta] = KM^a$*

Polymer	Solvents		A_2	a
Polystyrene	Chloroform 74.5	Methanol 25.5	0	0.65
Polystyrene	Dioxane 78	Methanol 22	0	0.65
Polymethyl methacrylate	Dioxane 53	Cyclohexane 47	0	0.61

The same was shown for other systems as well. The authors say this is due to selective sorption by the coil of the solvent, which has greater affinity for the polymer. For example, the polystyrene coil selectively absorbs benzene from the benzene-methanol mixture. Therefore, the concentration of a solvent near the coil may be different from that in it. Near the coil, conditions may be realized that conform to $A_2 = 0$, while this is not so in it. Therefore, the coil is not in the unperturbed state, i.e., $a \neq 0.5$.

The average density of a polymer substance in a coil can be calculated when the dimensions of macromolecules are determined. For example, for the polyvinyl naphthalene fraction with $M_w = 2.4 \times 10^5$, $(\bar{h}^2_\theta)^{1/2} = 400$ Å, and the average density is 0.017 g/cm³. Since the partial specific volume of this polymer in solution $\bar{V}_{2\,sp} = 0.88$, the segments of the polymer chain occupy only 1.5 per cent of the coil volume. The remaining volume is occupied by the solvent molecules. Consequently, the volume of the swollen coil is considerably greater than the sum of all its segments. When we speak of the size of a macromolecule in a solution, we imply the size of the "effective" sphere, which depends on the quality of a solvent.

16.4. DETERMINATION OF THE SHAPE OF MACROMOLECULES IN DILUTE SOLUTIONS BY THE BIREFRINGENCE METHOD

16.4.1. Birefringence

Birefringence, or double refraction, is the phenomenon observed when a light beam passes through an optically anisotropic medium *. The incident light beam is resolved into two rays travelling at different speeds and polarized in two planes at right angles to each other.

Birefringence occurs when light passes through uniaxial crystals, i.e., crystals having a single optical axis, this being the direction in which there is no double refraction. Such are, for instance, Iceland spar crystals. In all other directions the light beam is resolved. If the light beam runs perpendicular to the crystal surface, one of the rays passes through without refraction, like in an isotropic medium, while the other is deflected. The former ray is called *ordinary*, and the latter *extraordinary*, because it does not obey the usual laws of refraction. If the light beam is obliquely incident on an Iceland spar crystal, the beam is also resolved, but both its components are refracted. One of the rays (the ordinary one) obeys the laws of refraction and its refractive index at any angle of incidence is 1.65 (for monochromatic sodium light). The second ray is the extraordinary one, and its refractive index depends on the angle of incidence.

Birefringence is determined by the difference in refractive indices of the extraordinary (n_e) and the ordinary (n_o) light rays:

$$\Delta n = n_e - n_o \tag{16.63}$$

In some cases, for example in Iceland spar, double refraction can be detected directly by the spatial divergence of the ordinary and extraordinary beams. If the spatial divergence of these beams is too small to be perceptible, birefringence can be detected by various polarizational and chromatic phenomena.

Optical anisotropy of a medium may be due to anisotropy of its component particles (atoms or molecules) and/or to their mutual arrangement. Thus, the hydrogen molecule is optically anisotropic, but owing to the disorderly arrangement of its molecules gaseous hydrogen behaves like an optically isotropic medium. In most cases optical isotropy of bodies is an average state stipulated by random arrangement of their component molecules. However, external influences may cause a rearrangement of their anisotropic elements, resulting in a macroscopic display of optical anisotropy.

* Optical anisotropy is the phenomenon of light travelling at different speeds in different directions.

That is why many bodies, in particular polymers, exhibit birefringence when strained.

For example, amorphous polymers in the absence of external effects are optically isotropic and do not exhibit birefringence. On deformation in the external mechanical field, they become optically anisotropic and exhibit birefringence. In the case of uniaxial extension (or contraction), the sample assumes the symmetry of an uniaxial crystal, whose optical axis coincides with the direction

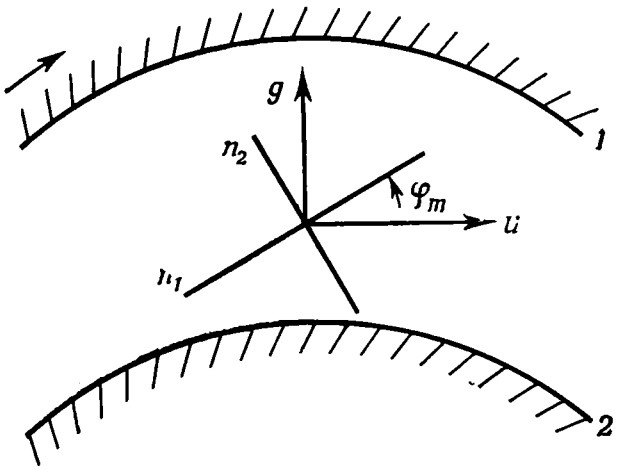

Fig. 16.12. Velocity vector of the translatory motion of particles and the velocity gradient in dinamo-optical measurements

of normal stress. Birefringence which originates is a function of tensile stress or unit strain λ.

$$\Delta n = \varepsilon \delta_s; \quad \Delta n = \gamma \lambda \tag{16.64}$$

The coefficients of ε and γ are known as the optical coefficients of stress and strain, respectively, while the phenomenon of birefringence in the case of polymer deformation is known as *photoelasticity*, or the *photoelastic effect.*

Birefringence in polymer solutions is exhibited only if they are acted on by the mechanical field, e.g., by shear stresses in the laminar flow. This phenomenon, known as *Maxwell's dynamo-optical effect*, was initially observed for rigid nonsymmetrical colloidal particles or suspension particles. The measuring devices are known as *dynamo-optimeters.*

The flow system under consideration is put in the gap between two coaxial cylinders, one of which is immobile, while the other rotates. Laminar flow is created in the gap. The rate vector is directed tangentially to the flow, and the rate gradient vector $\dot{\gamma}$ or g is directed radially (Fig. 16.12).

If rigid particles are spherical, birefringence is not observed in flow. But if the particles are asymmetrical, they orient by their

long axes towards flow. The orientation direction should coincide with the rate vector, but orientation is always upset by thermal motion. Therefore, the direction of the preferred orientation of particles with the direction of flow constitutes an angle φ_m, known as the *orientation angle*, or the *extinction angle* (Fig. 16.12).

Birefringence in the orientation of rigid particles is due to two causes: the intrinsic optical anisotropy of particles, which is caused by various indices of refraction of the particle in different directions, and the anisotropy of shape, which is exhibited when

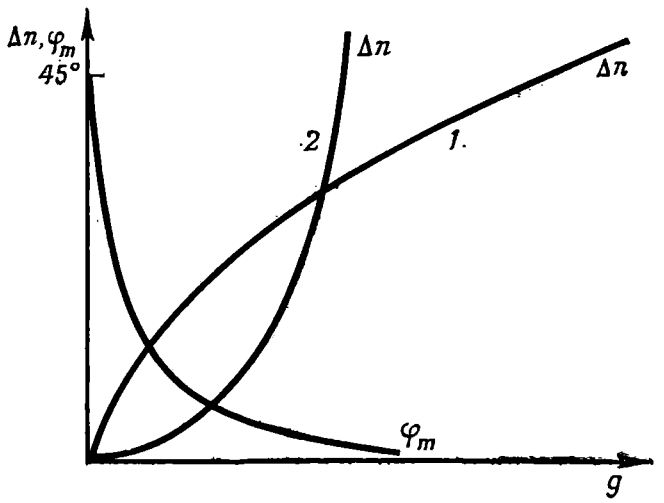

Fig. 16.13. Dependence of birefringence and extinction angle on the velocity gradient for rigid (*1*) and flexible (*2*) macromolecules

the average refraction index of a nonspherical particle differs from the refraction index of the environment.

Birefringence in flow is a property possessed by concentrated and dilute polymer solutions. It was studied in detail in respect of concentrated solutions by Philippoff, who at the same time investigated their rheological properties. Birefringence in the flow of dilute polymer solutions has been thoroughly studied by Tsvetkov, Frisman, and others.

Long chain macromolecules which are more or less coiled in dilute solutions not only orient, but also deform in laminar flow. It follows from experimental data that at high shear stresses, Maxwell's effect in polymer solutions is caused mainly by deformation of macromolecules. At low shear stresses, it may be caused by deformation and orientation. To ascertain the causes of birefringence, let us consider the dependence of Δn and φ_m on the rate gradient.

The dependence $\varphi_m(g)$ for chain molecules is qualitatively similar to that of rigid particles: as the rate gradient grows, the orientation angle diminishes from 45° to values which approxi-

mate 0° (Fig. 16.13). The dependence $\Delta n(g)$ for rigid particles differs from that for flexible-chain molecules. For rigid particles, which orient only in flow, the curves of $\Delta n(g)$ tend to saturation (curve *1*, Fig. 16.13). This dependence is linear at small rate gradients for solutions of flexible-chain polymers when the refraction indices of the polymer and of the solvent are equal; at high g, it is expressed by curves which are concave down to the ordinate (curve *2*, Fig. 16.13). Such a dependence indicates the deformability of macromolecules in flow, i.e., their kinetic flexibility.

The quantity Δn depends not only on the rate gradient, but also on the concentration of the solution and the viscosity of the medium. Therefore, the experimental data obtained at different g and c are usually extrapolated to zero concentration and to the zero rate gradient, and the *characteristic value of birefringence* or the *dynamo-optical constant* is obtained:

$$[\Delta n] = \left|\frac{\Delta n}{gc\eta}\right|_{\substack{c\to 0\\ g\to 0}} \qquad (16.65)$$

where η = viscosity of the medium
c = concentration.

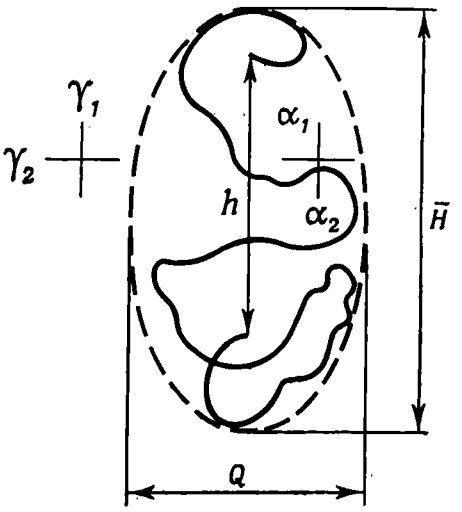

Fig. 16.14. Model of a chain molecule which is statistically coiled (explanation is given in the text)

The quantity $[\Delta n]$ is determined by the intrinsic anisotropy of macromolecules and the shape effect; a distinction is made between the macroshape effect and the microshape effect.

The *intrinsic anisotropy* of macromolecules is characterized by the difference in the main polarizabilities γ_1 and γ_2 (Fig. 16.14). It depends on the anisotropy of segments and monomeric units. *Segmental anisotropy* implies the difference in polarizabilities along and across its axis, $\alpha_1 - \alpha_2$. The measure of the *optical anisotropy of the monomeric unit* is the difference in its polarizabilities in parallel and perpendicular directions to the chain, $a_\parallel - a_\perp$.

The macroshape effect is caused by the asymmetry of the coil shape, i.e., by a deviation of the equilibrium form of a coil from the spherical one. Therefore $\gamma_1 \neq \gamma_2$, and optical anisotropy appears. It is precisely this effect that reflects the coil shape and is connected with the so-called shape factor $p = \frac{\bar{H}}{\bar{Q}}$, where $\bar{H}$ and $\bar{Q}$ are the average length and cross section of the coil, respectively.

The *microshape effect* is caused by the anisotropic distribution of segments in the Gaussian coil.

Theoretically, the characteristic value of birefringence of a polymer solution is the sum of three effects: intrinsic anisotropy of a chain $[n]_l$, the macroshape effect $[n]_f$ and the microshape effect $[n]_{fs}$:

$$[\Delta n] = [n]_l + [n]_f + [n]_{fs} \tag{16.66}$$

$$[n]_l = \frac{4\pi}{45kT} \frac{(n_s^2+2)^2}{n_s} [\eta]_0 (\alpha_1 - \alpha_2) \tag{16.67}$$

$$[n]_{fs} = \frac{(n_s^2+2)^2 (n_k - n_s)^2 [\eta]_0 M_0 s (L_2 - L_1)_s}{180\pi RTn_s^2 d} \tag{16.68}$$

For any ellipsoidal hydrodynamically impermeable macromolecule, regardless of whether it is a Gaussian chain or not, the anisotropy of the macroshape is as follows:

$$[n]_f = \left(\frac{n_s^2+2}{3}\right)^2 \frac{M}{120\pi d^2 RT} \frac{(n_k^2 - n_s^2)^2}{n_s^3} [b_0 f_0 (L_2 - L_1)] \tag{16.69}$$

where $[\eta]_0$ = intrinsic viscosity at $g \to 0$

n_s and n_k = indices of refraction of the solvent and the polymer, respectively

d = density of the dry polymer

M = its molecular mass

M_0 = molecular mass of the monomeric unit

s = number of monomeric units in the statistical segment

k = Boltzmann constant

$(L_2 - L_1)$, b_0 and f_0 = parameters depending on the shape factor of the coil p.

16.4.2. Segmental Anisotropy

It follows from Eqs. (16.67)-(16.69) that in the presence of the macro- and microshape effects, birefringence of polymer solutions should depend on the index of refraction of a solvent, and this has been confirmed experimentally in many works. The parabolic dependence of Δn on n_s (Fig. 16.15) was obtained in all cases according to the equations. The minimum of the parabola corresponds to the solution for which the shape effect is null. The value of Δn obtained in this case is determined by the intrinsic anisotropy of polymer macromolecules.

Hence, if measurements are taken of birefringence of solutions of polymers in a solvent whose refractive index is equal to that

of a polymer, the macro- and microshape effects would be absent, and Eq. (16.67) can be used to calculate $\alpha_1 - \alpha_2$. For this purpose, it is necessary to study the concentration dependence of Δn and viscosity η, and extrapolate to zero concentration, i.e., obtain the values of $[\Delta n]$ and $[\eta]$.

A simpler method proposed by Peterlin is widely used for solutions of polymers with flexible chains. According to this method, experimental data obtained for solutions of different concentrations at $g \to 0$ are plotted as value of *specific birefringence* $\frac{\Delta n}{g(\eta - \eta_0)}$ that depends on concentration, where η and η_0 are the viscosities of the solution and the solvent, respectively. A typical graph of such a dependence is given in Fig. 16.16. As we see, the points lie on one straight line parallel to the abscissa axis, regardless of the molecular mass of a polymer and its polydispersion.

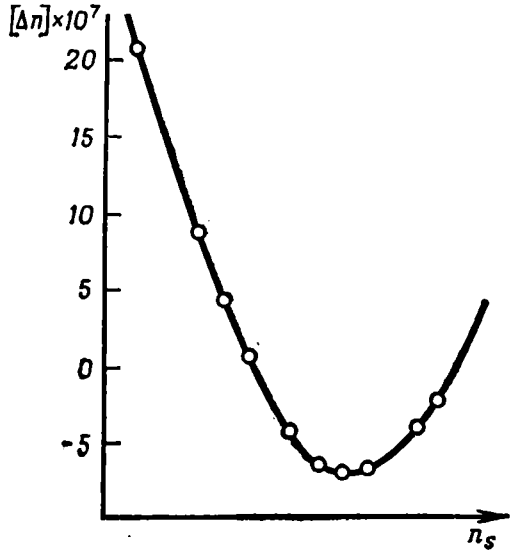

Fig. 16.15. Dependence of birefringence characteristic value on refractive index of a solvent

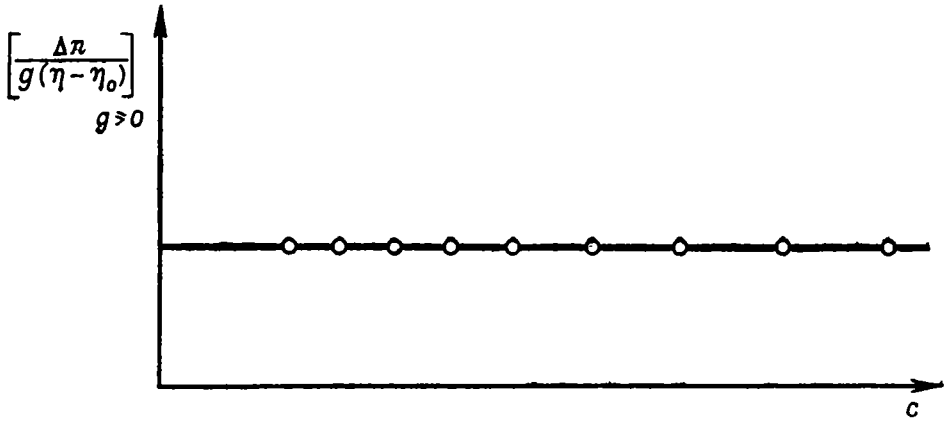

Fig. 16.16. Typical dependence of $\Delta n/g(\eta - \eta_0)$ on concentration of a solution

The section cut off by this line on the ordinate axis is used to calculate the value of $\alpha_1 - \alpha_2$.

16.4.3. Macroshape Effect

The macroshape effect can appear only when the indices of refraction of a polymer and of a solvent differ. A characteristic feature

of this effect is its dependence on the molecular mass of a polymer M, while the remaining two effects do not depend on M. Therefore, in order to calculate the macroshape effect, it is necessary to plot a graph of dependence of the total experimental quantity $\frac{[\Delta n]}{[\eta]_0}$ on $\frac{M}{[\eta]_0}$ for several fractions of some polymer in a definite solvent (Fig. 16.17). The points lie on a straight line, whose slope is $\frac{[\Delta n]_f}{M}$. The section which it cuts off on the ordinate axis can

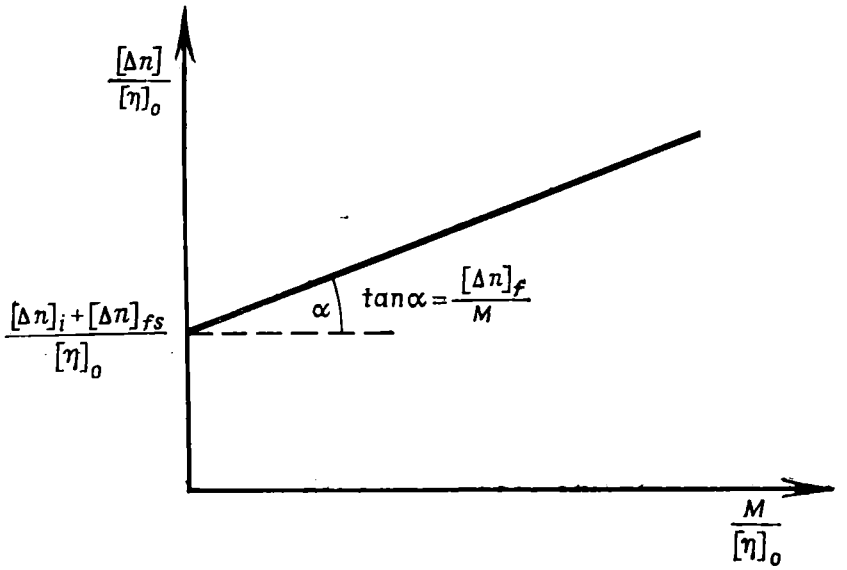

Fig. 16.17. Graphical illustration of macroshape effect (explanation is given in the text)

be used to determine the sum of $[n]_i$ and $[n]_{fs}$. Knowing $[n]_f$, one may use Eq. (16.69) to calculate the quantities b_0, f_0 and $(L_2—L_1)$, and by respective equations the shape factor p is found. The parameter p can change in a wide range, from $p \cong 2$ for the Gaussian coils to $p = 20$ for rigid rod-like molecules.

16.4.4. Microshape Effect

It follows from Fig. 16.17 that the straight line cuts off the quantity $\frac{[n]_i + [n]_{fs}}{[\eta]}$ on the ordinate axis. Consequently, we can determine the microshape effect $[n]_{fs}$ if we know the total value of $[\Delta n]$ and the value of segmental anisotropy $[n]_i$, which is determined in separate experiments for solutions of the given polymer in the way described on page 521. The effect also does not depend on the molecular mass, and it is very small for flexible-chain polymers of high molecular mass. Therefore, it is usually neglected.

Conversely, this effect is very considerable for chains of great equilibrium rigidity.

16.5. DETERMINATION OF EQUILIBRIUM FLEXIBILITY (RIGIDITY) OF POLYMER CHAINS

Equilibrium of thermodynamic flexibility of a polymer chain is estimated by the value of the thermodynamic segment, or Kuhn's segment A (p. 101), which can be calculated from experimental data on the dimensions of molecules and segmental anisotropy.

Hence, theoretically, the root-mean-square end-to-end distance of chains determined in the θ-solvent, $\bar{h}_\theta^2$, is connected with the quantity A by the equation

$$A = sl_0 = \frac{\bar{h}_\theta^2}{L} \tag{16.70}$$

where s = number of monomeric units in the segment
L = hydrodynamic length of the completely extended chain
l_0 = length of the monomeric unit in the direction L.

Consequently, after determining $\bar{h}_\theta^2$ experimentally from data on light scattering (p. 512), Eq. (16.70) can be used to calculate s and A.

These parameters can be calculated also by data on segmental anisotropy $(\alpha_1 - \alpha_2)$, which is measured by the method of birefringence in flow (p. 517).

As we have seen, the quantity $(\alpha_1 - \alpha_2)$ does not depend on the molecular mass of a polymer, and it is a characteristic of the microstructure of a chain. It is connected with the anisotropy of the monomeric unit by the simple relation

$$(\alpha_1 - \alpha_2) = s(a_\parallel - a_\perp) \tag{16.71}$$

where s = number of units in the segment.

Knowing $(\alpha_1 - \alpha_2)$ and s, one can use Eq. (16.71) to determine the anisotropy of the monomeric unit $(a_\parallel - a_\perp)$. However, this quantity is usually calculated by known data on the polarizability of valency bonds. Depending on the nature of these bonds, the quantity $a_\parallel$ along the chain and in side substituents may be greater or less than $a_\perp$, and therefore their difference may be a positive or negative quantity (Table 16.2). For example, the introduction of aromatic rings or ONO_2 groups as substituents leads to negative values of $(a_\parallel - a_\perp)$. The sign of $a_\parallel - a_\perp$ determines the sign of segmental anisotropy, which can also be positive or negative.

Knowing $(\alpha_1 - \alpha_2)$ and $(a_\parallel - a_\perp)$, one can calculate by Eq. (16.71) the number of units in the segment s, i.e., chain rigidity can be estimated.

For rigid-chain macromolecules, when the microshape effect is exhibited, the parameter s can also be calculated by Eq. (16.68).

TABLE 16.2. *Anisotropy of Segment* $(\alpha_1 - \alpha_2)$, *Monomeric Unit* $(a_\parallel - a_\perp)$ *and Rigidity of Macromolecules of Some Polymers*

Polymer	Solvent	$\alpha_1 - \alpha_2$, 10^{25} cm^3	$a_\parallel - a_\perp$, 10^{25} cm^3	s	A, Å
Polydimethyl siloxane	Benzene	+4.7	0.96	4.9	14.0
Polyethylene	Xylene	+50	+7.3	7.0	20.8
Polyisobutylene	Benzene	+50	+8.2	6.0	18.3
Polystyrene (atactic)	Bromoform	−145	−18.0	8.0	20.0
Polymethyl phenylsiloxane	Benzene	−66	−13.5	4.9	14.0
Ethyl cellulose	Tetrachloroethane	430	21	20	200
Cellulose nitrate	Cyclohexanol	−300	−18	16	200

The equilibrium rigidity of a flexible polymer chain is estimated, as indicated above, by the ratio of the root-mean-square distance measured in the theta solvent to the quantity $(\bar{h}^2_{fr})^{1/2}$ of the free-linked chain $(\bar{h}^2_\theta)^{1/2}/(\bar{h}^2_{fr})^{1/2}$. All these parameters for some polymers are given in Table 16.2.

It follows from the table that the value of segmental anisotropy can change in a very wide range. Small values of $(\alpha_1 - \alpha_2)$ characterize, as a rule, the low equilibrium rigidity of a chain. The values of s and A are not great in this case: for polymers having equilibrium-flexible chains, A lies in the range of 14-20 Å.

The high values of $(\alpha_1 - \alpha_2)$ may be due either to a high value of $a_\parallel - a_\perp$ or to a great value of s, i.e., to high chain rigidity. For example, $a_\parallel - a_\perp$ for ethyl cellulose is comparatively small, while $\alpha_1 - \alpha_2$ is a very large quantity. Therefore, $A = 200$ Å. Such values of A are characteristic of moderately rigid polymers, including cellulose and its esters. It follows from the table that there are polymers whose equilibrium rigidity is considerably greater ($A = 1000$-2400).

16.5.1. Effect of Solvents on Flexibility of Polymer Chains

Until the mid-1960's, there were two viewpoints concerning the effect of a solvent on the equilibrium rigidity of a chain. Some researchers believed that the solvent affects only the dimensions of molecular coils, and that the equilibrium rigidity of a chain did not depend on the quality of a solvent. Others held that the solvent should affect the flexibility of a polymer chain.

The effect of a solvent on the value and sign of segmental anisotropy of many polymers was shown for the first time by

E. V. Frisman and coworkers. Later, this was detected also by other researchers, and it is now obvious that the rigidity of a polymer chain can considerably change under the action of a solvent. For example, Kuhn's segment of cellulose tributyrate is considerably greater in its solutions in bromoform than in tetrachloroethane, and this change in A is caused by a change in the rigidity of the macromolecule.

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CHAPTER 17

Structure of Solutions and Gels of Polymers

Polymeric articles are often moulded through solutions or gels, and the structure of the latter determines to a considerable extent the structure of the polymeric articles being moulded (fibres, films, lacquer coats, etc.). Therefore, the study of the structure of a solution is no less important than the study of the structure of a polymer itself.

The structure of polymer solutions should be studied from the same standpoint as the structure of liquids and liquid solutions of low-molecular substances (LMS), when most of the information is obtained on the basis of small-angle X-ray scattering, Rayleigh light scattering, viscosity, dielectric relaxation, nuclear magnetic resonance, thermodynamic investigations, infrared spectroscopy, and so forth.

All these studies have shown that the structure of each of two liquids changes when they are mixed together. This is exhibited especially clearly in respect of the most structuralized liquid, water, whose structure may become ordered or disordered, for example, when various ions are introduced into it. This so-called positive or negative hydration results in positive or negative viscosity (the viscosity of water increases or decreases). The translatory motion of water molecules and relaxation time then change. Similar phenomena are observed in water-alcohol solutions. When in a solution there is a large amount of water, the structure of the latter is mainly preserved, and alcohol molecules are introduced into it rather easily. But the introduction of water molecules into alcohol changes its structure, and structures consisting of molecules of both components are formed in the central regions of the concentration.

The components change structurally also in non-aqueous solutions. In this case, the phenomena of a preferential interaction

between unlike molecules (solvation) or similar ones (association) are observed, depending on the degree of affinity between the components. Both phenomena change mobility and relaxation time. Thus, solvates and associates are elements of the structure of a solution, just as concentration fluctuations, which are their nuclei.

When polymers dissolve, the structure of both components also changes and the phenomena of solvation and association are observed.

17.1. SOLVATION IN POLYMER SOLUTIONS. METHODS OF DETERMINING THE THICKNESS OF A SOLVATE LAYER

Solvation in polymer solutions began to be studied long ago, when they were still considered to be lyophilic colloids. After studying the osmotic pressure and viscosity of dilute polymer solutions, researchers drew the conclusion that there are polymolecular solvate layers around polymer micelles. Several authors had estimated that the amount of a solvent in a solvate layer was greater than its total amount in a flask. Such absurd conclusions were made because the methods used could not in principle indicate the amount of the solvent that is firmly bound with a polymer.

In polymer solutions, the phenomenon is observed to which Mendeleyev drew attention when he was studying the aqueous solutions of alcohol and sulphuric acid. He showed that not all water is retained equally firmly by a solute, as a result of which some water is separated from sulphuric acid solutions very readily at 100 °C, while a small part of it is retained by the acid even at 300 °C. Stable hydrates having the composition of $C_2H_5OH \cdot 3H_2O$ are formed in alcohol-in-water solutions, while water which is not included in the hydrate is infirmly bound with alcohol. "The force acting in solutions consequently has different intensity".

In polymer solutions, a part of a solvent is also bound more firmly with a polymer than another, and this gave rise to the terms "bound" and "free" solvents, i.e., solvents which are and are not in the solvate layer.

The amount of a bound solvent, i.e., a solvent which solvates a polymer, can be estimated by several methods which give information on either the strength of a bond or the mobility of molecules. They are methods of thermochemistry (heats of dilution and heat capacity), compressibility, dielectric relaxation, nuclear magnetic resonance, and so forth.

17.2. DETERMINATION OF AMOUNT OF BOUND SOLVENT (OR PLASTICIZER) BY HEATS OF DILUTION OR HEATS OF SORPTION

The determination of the integral heat of dilution (p. 396) of a polymer in a large amount of a solvent cannot indicate the thickness of the solvate layer, because the number of molecules of the absorbed solvent that corresponds to the measured heat effect is unknown. This task can be tackled by determining the integral heats of dilution (p. 396) or the heats of sorption.

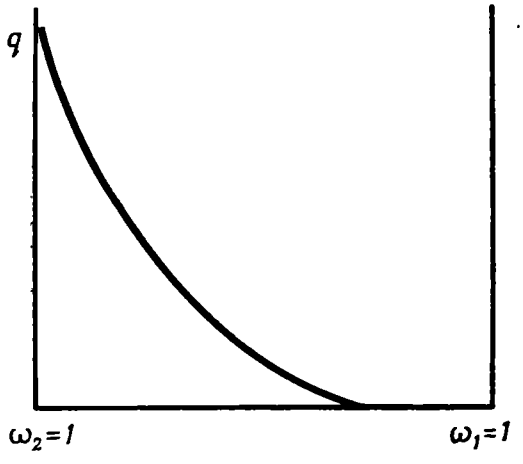


Fig. 17.1. Dependence of integral heats of dilution on weight fraction of a solvent in a solution being diluted

The **first technique,** applied for the first time by Rodewald and then widely used by Dumansky and his coworkers, consists in the measurement of the integral heats of dilution q of preliminarily prepared polymer solutions containing various weight fractions ω_1 of the same solvent. As ω_1 increases in a preliminarily prepared solution, the number of the functional groups of a polymer that have not reacted with it decreases. Therefore, the integral heat of dilution diminishes to zero (Fig. 17.1).

The part of a solvent that interacts with a polymer with heat liberation is known as a "bound" solvent. The remaining part of the solvent absorbed by the polymer interacts with it without the heat effect, and it is a "free" solvent.

The **second technique,** proposed by Kargin and Papkov, consists in the study of the sorption of a solvent on a polymer from its solutions in a liquid with which the polymer practically does not interact, such as the sorption of acetone on cellulose nitrate (CN) from its solutions in *n*-pentane. It is preliminarily ascertained that *n*-pentane (or some other liquid) is practically not sorbed by CN, and the heat of wetting is very small ($\sim$0.3 cal/g). The isotherms of sorption of acetone on CN are plotted and the heat of sorption of acetone on CN from the solutions of the same concentration is measured simultaneously. Consequently, the number of molecules of the absorbed solvent to which the measured heat effect corresponds is known.

It was shown by both methods that one gram of a polymer absorbs with the liberation of heat, at the most 0.5 g of a solvent;

for example, one gram of CN strongly binds 0.473 g of acetone. The authors assumed that acetone molecules are sorbed by ONO_2 groups of CN *. Taking into account that CN used in work had about 10 per cent of N_2, they calculated the number of grams of acetone for the main unit of a polymer and showed that there is one molecule of acetone per ONO_2 group. Consequently, a monomolecular solvate layer is formed.

Determination of the Amount of a Bound Solvent by the Method of Studying the Compressibility of Solutions. This method was first applied to polymer solutions by Pasynsky. Liquids and liquid solutions have comparatively low compressibility, which is the smaller, the greater is the uniform pressure that acts on a liquid. For a number of liquids at a pressure of 12 000 atm, the coefficient of isothermal compressibility β_T averages 6-7 per cent of the value of the coefficient of compressibility at atmospheric pressure.

Ions and even dipoles create electric fields of enormous intensity that are equivalent to very high pressures calculated by the equation

$$p_{dip} = \frac{\varepsilon' - 4}{4\pi\varepsilon'^2} \frac{\mu^2}{r^6} \qquad (17.1)$$

where μ = dipole moment
ε' = dielectric constant of a medium
r = distance from the dipole.

It follows from Eq. (17.1) that the quantity p sharply decreases with an increase in r, as we can see below:

r	Å	1	3	5	10
p_{dip}	atm	79 000	975	126	7.9

The pressure of the electric field is very high in the immediate proximity of the dipole, and therefore the liquid layer adjacent to the dipoles is highly compressed. The coefficient of compressibility of this layer β_T must be considerably less than β_0 of the liquid itself. As the distance from the dipole increases, field pressure increases and value β grows. Since the curve of the relation $p = f(r)$ is very steep, the real solvate sphere with the changing compressibility coefficient can be approximately replaced by the effective, *noncompressible solvate volume*, which is in the immediate proximity of the dipole, and it can be assumed that the coefficient of compressibility of a liquid has a normal value of β outside this volume.

If α is the amount of a solvent in a noncompressible solvate layer, $(1 - \alpha)$ is the amount of the remaining solvent ("free"

* This assumption is not quite correct, because acetone molecules can be absorbed also by OH groups of cellulose which is not completely etherified.

solvent). Then $\beta = \beta_0(1 - \alpha)$ and

$$\alpha = \left(1 - \frac{\beta}{\beta_0}\right) \tag{17.2}$$

If 100 g of a solution contain m grams of a dissolved polymer and $(100 - m)$ grams of a solvent, the amount of the noncompressible solvent is expressed by the product $(100 - m)\left(1 - \frac{\beta}{\beta_0}\right)$. Hence, the amount of grams of a solvent bound by one gram of a solute is

$$h = \frac{(1 - \beta/\beta_0)(100 - m)}{m} \tag{17.3}$$

17.3. DETERMINATION OF THE AMOUNT OF BOUND SOLVENT BY THE METHOD OF DIELECTRIC RELAXATION

The method was first used for this purpose by Marinesco, who proceeded from the simple assumption that the mobilities of molecules of bound and free solvents should differ. Indeed, if the dipoles of a solvent are firmly retained in the solvate layer, they are fixed, as it were, and they cannot rotate in the external electric field. Therefore, the dielectric constant of a polymer solution is less than ε' of a pure solvent. He represented the total specific polarization of one millilitre of a solution $P_{1,2,3}$ in water by an additive sum of three summands:

$$P_{1,2,3} = P_1 n_1 + P_2 n_2 + P_3 n_3 \tag{17.4}$$

where n_1 = number of grams of free water
n_2 = number of grams of bound water
n_3 = number of grams of a polymer that is contained in one millilitre of a solution
P_1, P_2 and P_3 = their specific polarizations, respectively, which are calculated by the equation

$$P = \frac{\varepsilon' - 1}{\varepsilon' + 2} \cdot \frac{1}{d} \tag{17.5}$$

where d is the density of a component. In calculating P of free water, the value of $\varepsilon' = 81$ is taken, and for bound water, $\varepsilon' = 2.2$ (ε' of ice) is taken. For a polymer, use is made of the value of ε' that is measured for the solid state.

The polarization of one millilitre of a solution is calculated by the equation

$$P_{1,2,3} = \frac{\varepsilon' - 1}{\varepsilon' + 2} \tag{17.6}$$

where ε' is the value of the dielectric constant of a solution that is being measured. Taking account of the total amount of water

contained in one millilitre of a solution, $S = n_1 + n_2$, the author obtained the equation

$$P_1(S - n_2) + P_2 n_2 + P_3 n_3 = \frac{\varepsilon' - 1}{\varepsilon' + 2} \tag{17.7}$$

Hence, the number of grams of water bound with one gram of a polymer

$$h = \frac{n_2}{n_3} = \frac{P_1 S + P_2 n_2 + \dfrac{\varepsilon' - 1}{\varepsilon' + 2}}{n_3 (P_1 - P_2)} \tag{17.8}$$

All measurements were made in the high frequency range, and, for proteins (haemoglobin, gelatin, etc.), the estimated values of h were in the range of 0.5-2.5 g per gram of a polymer.

17.4. CONCEPTS OF SOLVATION IN POLYMER SOLUTIONS AND THEIR FURTHER EVOLUTION

The works expounded above served as the basis for definite concepts of solvation in polymer solutions, which arose in the late 1930's and which can be formulated in the following way: a part of the solvent that is contained in a solution is strongly retained by a polymer, forming a solvate layer, or a "bound" solvent. The remaining part of the solvent is retained by the polymer considerably weaker, and it constitutes the "free" solvent. The amount of the bound solvent is the larger, the greater is the polarity of the functional groups of a polymer and their ability to form hydrogen bonds. For example, it constitutes 31-43 per cent of the mass for CN solutions. Up to 60 per cent of water may be contained in the solvate layer for aqueous solutions of poly(vinyl alcohol) or proteins, i.e., where strong hydrogen bonds may be formed (there are 72 g of H_2O per 44 g of PVA). This means that, for example, the entire solvent present in 40 per cent solutions of polar polymers is bound, and there is no free solvent in them at all. A free solvent may appear only when a solution is diluted further. A bound solvent differs by its properties from a free one. It is more oriented, ordered and compressed than a free solvent, and its molecules are less mobile. Consequently, the solvent, while penetrating into a polymer and destroying its structure, changes also its own structure under the action of the polymer.

These concepts were later confirmed by many researchers who used up-to-date methods.

For example, the flow birefringence method was used to show that a solvent is oriented even in very dilute polymer solutions. This method makes it possible to estimate the optical anisotropy of a segment, which is the difference in its polarizabilities in di-

rections parallel and perpendicular to the chain ($\alpha_{\parallel} - \alpha_{\perp}$) (p. 517).

The intrinsic optical anisotropy of segments was calculated for many polymers, and it was believed for a long time that this anisotropy depended on the skeleton of a chain and on the nature of side substitutes, and did not depend on the nature of a solvent and on temperature. Frisman and his coworkers used the solutions of various polymers to convincingly show that the value and sign of segmental anisotropy depended on temperature and the thermodynamic interaction between a polymer and a solvent. They said that the results obtained were due to the origination of the orientation order of solvent molecules in the immediate proximity of a polymer chain. It was shown that even a very insignificant degree of orientation of solvent molecules causes a considerable change in segmental anisotropy.

Thus, a solution of any concentration, even of infinite dilution, has short-range solvation, i.e., a polymer affects the structure of the neighbouring medium.

Dielectric relaxation and nuclear magnetic resonance techniques were used to convincingly show that bound and free solvents have different mobilities.

For example, Sillarce showed as early as 1939 that, in order to study the specific features of the structure of a low-molecular substance (LMS), it should be put in a nonpolar solid matrix, such as highly viscous paraffin wax. This method was evolved further by Devis and his coworkers and Borisova and her coworkers. To study the processes occurring in the polymer-LMS system in a wide range of concentrations and temperatures, the main matrix used was glassy polystyrene (PS), which does not exhibit dielectric losses in the range of (—120°)-(—130°) C. Therefore, the appearance of dipole relaxation in this range of temperatures and frequencies used can be associated only with the motion of LMS. It was ascertained as a result of such investigations that, as the content of the polar component in the PS matrix grows, the relaxation time τ of dipole polarization increases, attains the maximum value, and then decreases. Such an extremum made of the change in τ is caused by the competing influences of two factors: (1) the orientation and association of LMS molecules, causing an increase in τ, and (2) the destruction of the polymer structure, resulting in an increase in the mobility of LMS molecules and a decrease in τ. These data show that LMS can move in a polymer matrix even at very low temperatures, and this is confirmed when such systems are studied by nuclear magnetic resonance method.

The phase state of bound and free solvents is sometimes debated in literature. This question should be solved on the basis of the

general thermodynamic and structural concepts of the phase given in Chap. 6. A solution or a plasticized system has only one phase at temperatures higher than the temperature of crystallization of a solvent or a plasticizer and higher than the temperature of phase separation. Notwithstanding the difference in the mobility and ordering of molecules of bound and free solvents, they do not represent separate phases in such systems. Moreover, there is no pronounced difference between bound and free solvents owing to the existence of short-range and long-range solvation: the molecules of a solvent can pass over to the solvate layer and come out of it under the action of thermal motion even at constant temperature. Therefore, it would be more correct to speak of the average degree of solvation.

The polymer-LMS system is a two-phase one in the region of temperatures and compositions where the liquid-liquid separation of a system takes place or a solvent (plasticizer) crystallizes.

17.5. ASSOCIATION IN POLYMER SOLUTIONS

Macromolecules do not interact with one another in very dilute polymer solutions, where they are sufficiently away from one another. Such isolated macromolecules can have different conformations (p. 97). If a macromolecule is flexible, it has the conformation of a random coil, which swells to a certain extent in a solvent, depending on the solvent quality and on temperature. This is characteristic of nonpolar or low-polarity polymers. Highly polar polymers and particularly polymers capable of forming interchain hydrogen bonds (rigid-chain polymers, biopolymers) have the conformations of helixes, rods and crankshafts in dilute solutions (p. 98).

When the concentration of a solution increases, macromolecules begin to come into contact with one another, forming associates. The higher the molecular mass of a dissolved polymer, the smaller is the concentration at which they come into contact; for substances of a very high molecular mass, associates are observed when concentrations are extremely small. This is exhibited in very high values of a molecular mass, which is measured by ordinary techniques (Chap. 16) and is the molecular mass of an associate.

Associates are statistical fluctuational formations which originate in a one-phase system. Their lifetime depends on the ratio of the energies of thermal motion and interchain interaction. Therefore, it is natural for more stable associates to originate in solutions of polymers that are capable of forming hydrogen bonds, in poor solvents, which cannot destroy these bonds, such as in solutions of poly(vinyl alcohol) in water, cellulose acetate and poly(vinyl chloride) in many solvents. So the value of the molecular

mass of methyl cellulose in a poor solvent can be 25 times greater than in a good one, in which associates are destroyed.

Association is observed also in respect of nonpolar polymers, such as rubber, in dilute solutions in poorer solvents in general, the decrease of solvent quality promotes the formation of associates.

As concentration grows, the size of associates increases and they interact with one another, forming supermolecular structures of greater complexity. Various methods give information on this.

17.6. ELECTRON MICROSCOPY

The electron microscope is a high-vacuum apparatus (p. 112) in which a solvent evaporates. Therefore, in order to study the structure of the solutions and gels of polymers, use is made of either electron microscopes having a freezing device or special techniques of preparation of the objects.

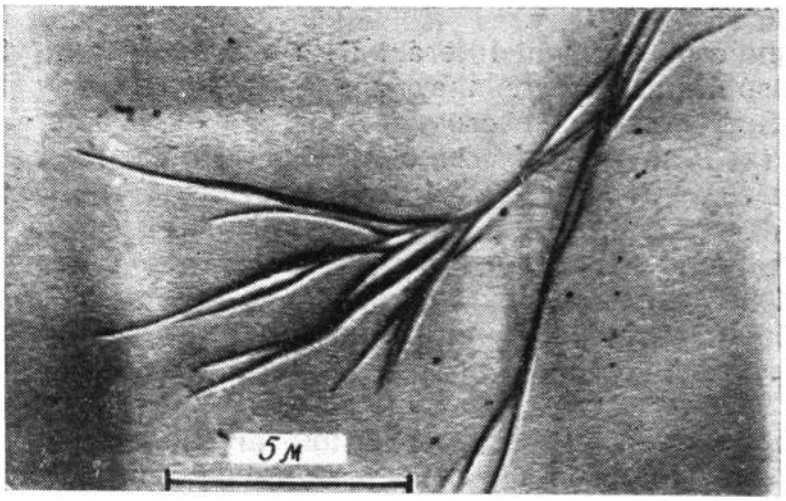


Fig. 17.2. Micrograph of a 0.2 per cent solution of poly-α-butylene in propan

The method of freezing a solution was used by Rucher who showed that there are separate macromolecules coiled into balls in very dilute solutions of some polymers (whose concentration is of the order of 10^{-3}-10^{-4} per cent). However, on freezing, a solvent may become crystallized, and this gives distorted results. Therefore, Kargin and coworkers proposed methods involving the use of either a solvent which becomes glassy or a solvent which has a very low critical temperature of the liquid-vapour transition. In the first method, the solvent is a substance whose glass-transition temperature is higher than room temperature and which readily becomes glassy on cooling. After a polymer completely dissolves

in such a solvent on heating, the solution quickly cools to a temperature which is lower than the glass-transition temperature of a solvent. In this case, homogeneous glass, in which the structure of the initial polymer solution is frozen, is obtained. Brittle fractures are then made from this glass by means of a thin needle,

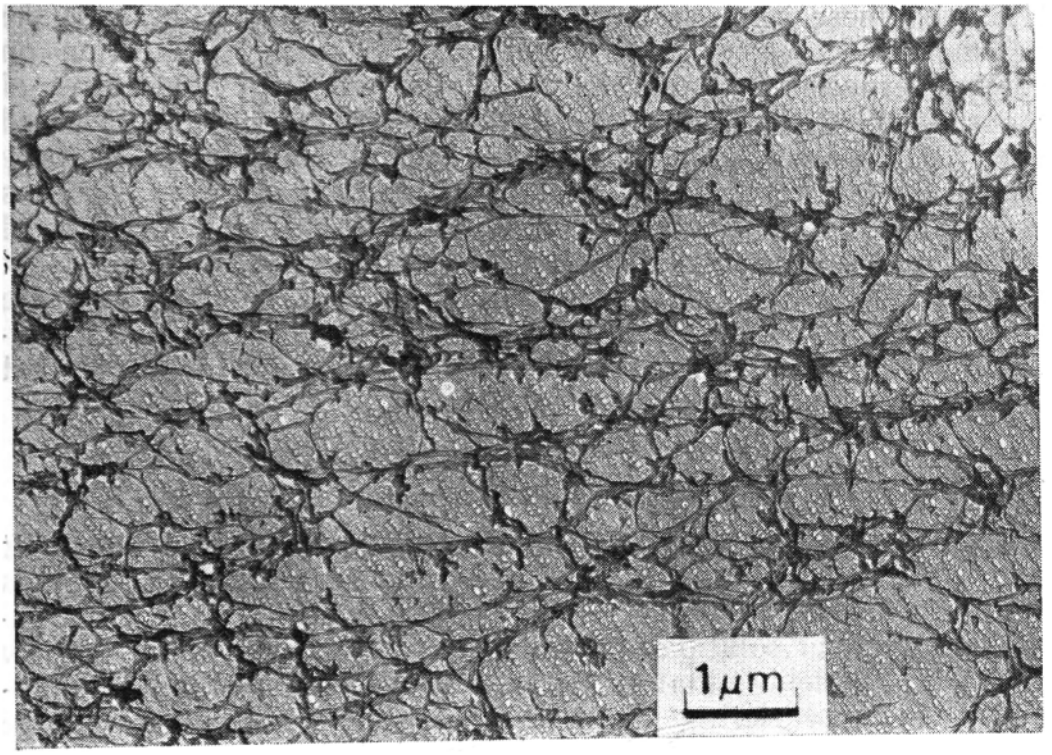


Fig. 17.3. Micrograph of a gel

and their surface is studied by the replica method (Chap. 5). Colophony, Novolak (phenol-formaldehyde) oligomers, and other substances were used as solvents which become glassy.

The second method, worked out for the first time for preparing biological suspensions, envisages the replacement of one solvent by another having a lower critical temperature. Kargin and coworkers had improved this method for preparing polymer objects. Compounds of low critical temperature, such as propane, ethylene and ammonia, were used as solvents or systems under consideration. The solvent is condensed in a capillary, into which a polymer is put beforehand, and the capillary is sealed. The capillary is filled with a liquefied solvent in such a way that the volume of a system would not increase noticeably on subsequent heating above T_{cr}. The sealed glass capillary is heated in a special furnace to 20-25 °C above the critical temperature. In this case, a solution of a polymer in a gaseous solvent is obtained. The end of the

capillary is then cut off, and the solution is "shot" at a target, which is an electron microscopic grid having a screen deposited beforehand.

These methods were used to show that associates formed from extended chains originate in the solutions of several polymers having a concentration of the order of 0.1-1 per cent (Fig. 17.2). However, these methods as well have disadvantages, because the polymer-LMS system may come close to phase separation on cooling, especially in the vicinity of the critical temperatures of the solvent itself (Chap. 12). If this is so, the picture observed does not represent the arrangement of macromolecules at ordinary temperatures. Moreover, the method of electron microscopy makes it possible to study polymer solutions having a concentration of not more than 3 per cent. Present-day electron microscopes do not resolve solutions of higher concentration. But polymer gels are now being successfully studied by means of special electron microscopes. Figure 17.3 gives a typical micrograph of a gel that clearly shows a three-dimensional network.

17.7. SMALL-ANGLE X-RAY SCATTERING

The presence of a short-range order in liquid metals and their alloys, liquids having hydrogen bonds, and even in liquid paraffins has been proven by means of X-rays. X-ray diffraction investigations of polymer solutions are only beginning now. One of the few works in this field is that by Berry, who used the method of small-angle X-ray scattering to show the presence of a short-range order in concentrated solutions of a rigid-chain aromatic polymer. He writes that a supermolecular structure is formed as the concentration of a solution grows.

17.8. INVESTIGATION OF THE LIGHT SCATTERING IN POLYMER SOLUTIONS

This method is widely used for studying the structure of LMS solutions. Such investigations are being carried out by Roshchina and Boterei who have shown the ordering of the structure of liquid hydrocarbons and their solutions.

The basic principles of the Rayleigh light-scattering method are expounded in Chap. 16. It is also shown there that the intensity of scattered light, caused by concentration fluctuations, grows linearly with an increase in the concentration of a polymer (Eq. 16.13). But this holds only for very dilute solutions, while in a wide composition range the concentration dependence of the excess intensity of light scattering is expressed by curves having a maximum. This was shown for the first time by Debye and Bueche

for a solution of polystyrene in benzene, and then by Tager and Andreyeva for very many polymer solutions. The height of the maximum, the degree of its broadening and its position on the concentration axis depend on the molecular mass of a polymer, temperature and the thermodynamic quality of a solvent.

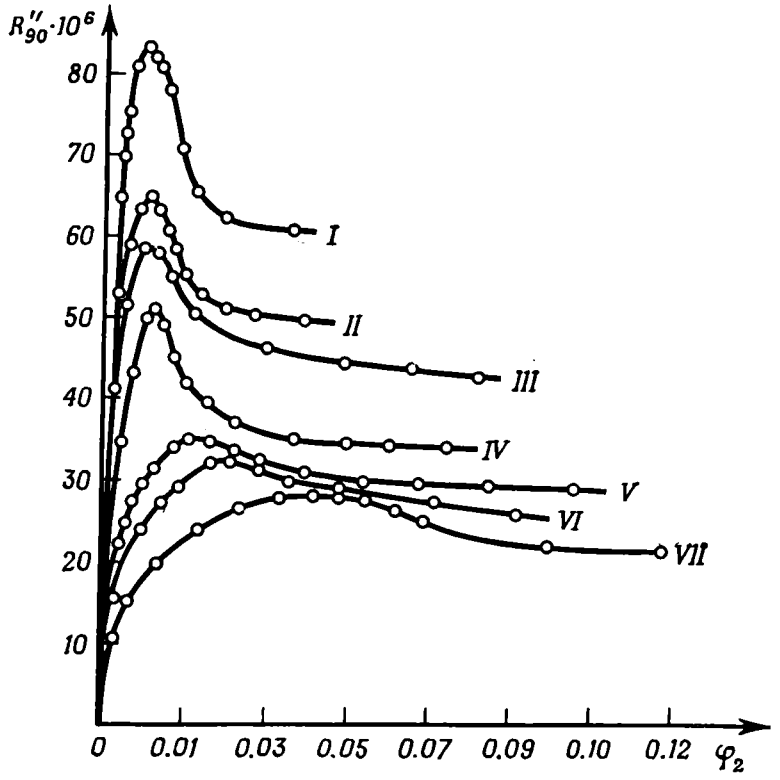


Fig. 17.4 Dependence of excess light scattering on the volume fraction of a polymer. Solutions of PS fraction in benzene:
I—$M=32\times10^5$; *II*—13×10^5; *III*—5×10^5; *IV*—2.5×10^5; *V*—10^5; *VI*—0.9×10^5; *VII*—0.3×10^5

The extremum character of this dependence, which resembles similar curves for liquid-liquid systems, is evidence of the fact that light scattering is caused not only by separate macromolecules, but also by their associates and more complex supermolecular structures, their size and degree of ordering. As the molecular mass of a polymer increases, the maxima of the curves shift towards the region of smaller concentrations, and the intensity of scattered light grows (Fig. 17.4). Consequently, the higher the molecular mass of a polymer, the smaller is the concentration at which associates are formed and the larger are their dimensions. For most solutions, the relation $R''_{90}=f(c)$ is expressed by curves having broad maxima; a sharp maximum is observed for solutions of PS in aromatic hydrocarbons.

The thermodynamic quality of a solvent is of very great importance. The worse is a solvent thermodynamically, i.e., the lower is its quality, the greater are the concentration fluctuations and the higher is the intensity of light scattering (Fig. 17.5*a*, *b*).

An elevation of temperature affects the magnitude of light scattering differently. For example, if the solvent capacity decreases with a drop in temperature and a system separates into phases on

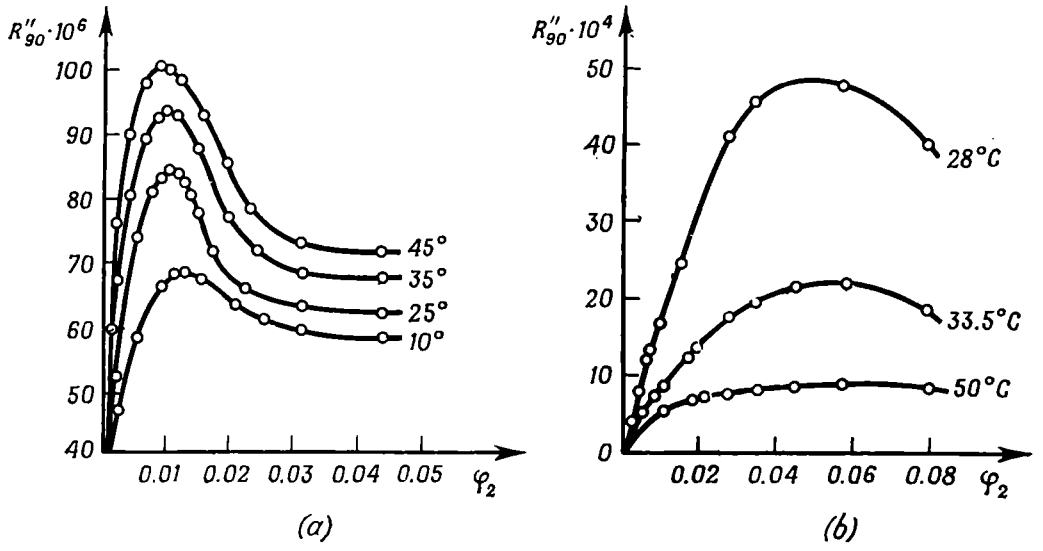


Fig. 17.5. Dependence of excess light scattering R''_{90} on the volume fraction of a polymer in a solution:

a—PS in a good solvent, benzene; *b*—PS in a poor solvent, cyclohexane

cooling, i.e., if it has the upper critical solution temperature (UCST), R''_{90} grows as temperature drops (Fig. 17.5*b*). This is observed for PS-cyclohexane and PS-decalin systems and other systems in the vicinity of UCST. If the solvent capacity decreases with an elevation of temperature and a system separates into phases on heating, i.e., if the lower critical solution temperature (LCST) is observed, the concentration fluctuations increase on heating, and this is accompanied with a growth in R''_{90} (Fig. 17.5*a*). For systems having UCST and LCST, R''_{90} grows both on heating and on cooling. Hence, the structure changes with a change in temperature and composition in homogeneous one-phase polymer solutions, and this is reflected also in a change in thermodynamic parameters (p. 371).

Concepts of the formation of supermolecular structures in polymer solutions were stated on the basis of such data.

17.9. VISCOSITY AND STRUCTURE OF SOLUTIONS

The viscosity of liquids is closely connected with their structure. Attention was drawn to this by Kobeko, and the interconnection between viscosity and the structure of low-molecular liquids is clearly shown in the works by Golik and his coworkers. Such an interconnection should exist also for polymer solutions.

Many attempts have been made to connect the value of intrinsic viscosity [η] with the degree of association of macromolecules. However, great care should be taken when the values of [η] are used for determining the increase or decrease of the degree of association, because the quantity [η] depends on the geometric

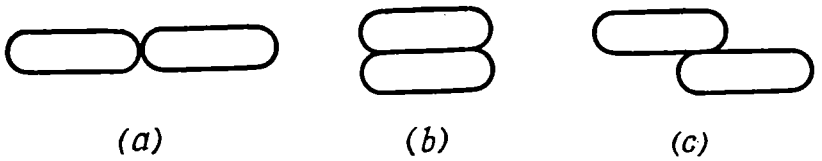


Fig. 17.6. Association of elongated particles of the type: *a*—"end-to-end", *b*—parallel arrangement of particles; *c*—intermediate case

arrangement of macromolecules in an associate. For example, Kuhn and Moser have theoretically shown that in the case of association of rods represented in Fig. 17.6*a*, the viscosity of a dilute solution increases, and in the case of association represented in Fig. 17.6*b*, it decreases. Viscosity may not change at all with an increase in the degree of association. There are also other indications of the insensitivity of intrinsic viscosity to association. This is very likely, because associates may be destroyed as a result of high rate gradients when dilute solutions flow.

But the initial Newtonian viscosity of concentrated solutions is very sensitive to a change in the structure of polymer solutions, and this was clearly shown by Tager, Dreval and coworkers. An elevation of temperature or the increase of the solvent capacity, promoting the destruction of a polymer, causes a decrease in the viscosity of a system. The lower are the temperature and the solvent capacity, the more strongly pronounced is structure formation and the greater is viscosity. The parameters of activation of viscous flow are structurally sensitive (Chap. 15).

A very characteristic feature is the change in the viscosity of a solution at the moment of its phase separation, when a new phase is formed in a one-phase solution. This occurs when a system approaches conditions which conform to the binodal as temperature and concentration change. This was shown for the first time when the temperature dependence of the viscosity of solutions of low-molecular liquids in the critical temperature range

was being studied. Semenchenko and Debye detected a sharp increase in viscosity with a subsequent drop (curve, in Fig. 17.7), i.e., a characteristic "surge" is observed on the viscosity polytherm. Later, such a phenomenon was detected also for polymer solutions, in the range of concentrations which correspond to the

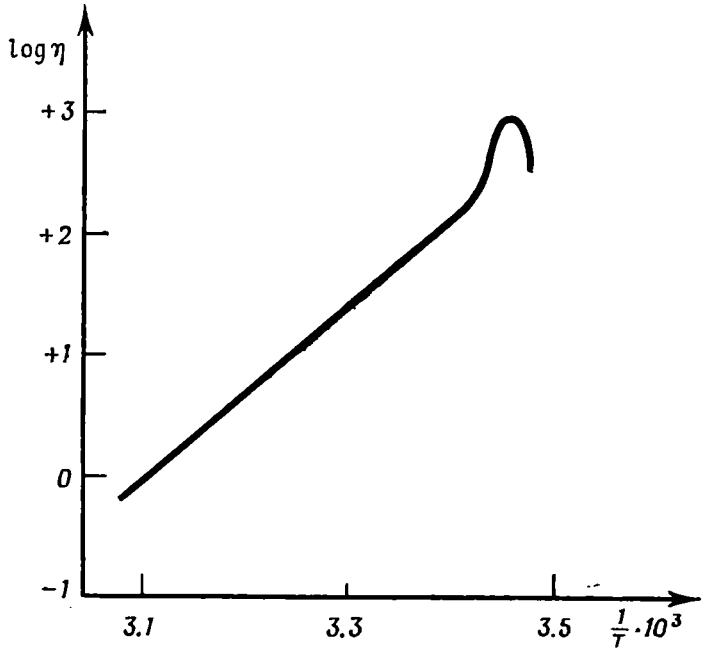


Fig. 17.7. Temperature dependence of viscosity for polymer solutions

phase separation of a system. A sharp increase in viscosity indicates intensively occurring processes of structure formation in a solution, while a drop in viscosity conforms to the separation of a system into two phases.

17.10. OTHER METHODS OF INVESTIGATING POLYMER STRUCTURES

Solutions of PS in benzene were recently studied by means of magnetic optical birefringence. Proceeding from the results obtained, it was concluded that such a solution has optically anisotropic diamagnetic aggregates of polymer chains.

Much information on the mobility of structural elements is given by the methods of dielectric relaxation, paramagnetic probe and nuclear magnetic resonance which can be used to estimate relaxation time (correlation time), i.e., the mobility of supermolecular structures. These methods were used to unequivocally show that the mobility of structural formations in solutions of polymers

in poor solvents is always less than in the medium of good ones. The formation of associates and solvates has been proven by infrared spectroscopy.

17.11. GENERAL CONCEPTS OF THE STRUCTURE OF POLYMER SOLUTIONS

The foregoing leaves no doubt that polymer solutions, like any liquid systems, are not structureless. The concepts of a polymer solution structure, which implies the mutual arrangement of molecules of both kinds and the conformation of macromolecules, are established now.

Very dilute solutions may contain isolated macromolecules of a more or less coiled or helical conformation that have swollen to a certain extent in a solvent, whose molecules are oriented near macromolecules.

Macromolecules begin to come into contact with one another in the region of high concentrations, which depend on the molecular mass of a polymer. At first, Bueche supposed that in this case macromolecules entangle one another, forming loops. This gave rise to the entanglement conception, which is widely used in various theories. This conception is similar to the concepts of entangled chains in amorphous polymers, which was acknowledged to be incorrect (Chap. 5). Ferry and his coworkers have experimentally shown in a series of works that the temperature dependence of viscosity and other rheological properties of solutions of several polymers contradict Bueche's model. They expressed the opinion that associates are formed in concentrated polymer solutions; these associates spread over comparatively large distances, and they originate not as a result of geometric entanglements, but as a result of intermolecular labile contacts, which are readily displaced, and this allows flow. Fox also believes that molecular chains cannot behave as cords which form loops, and when macromolecules come into contact, there should be ordinary intermolecular association by means of contacts between macromolecules. This is similar to Lodge's concepts of spatial fluctuational networks, which are formed and destroyed under the effect of thermal motion.

Since it has been experimentally ascertained that associates exist even in very dilute solutions, the opinion was expressed that fluctuational networks are formed not from macromolecules, but from associates which originated beforehand. This is in conformity with the concepts developed by Prince and his coworkers for polymer gels. They write that amorphous polymer networks are usually regarded as an ensemble of disorderly bound coiled chains. The real structure, however, may be considerably more complex,

and the existence of intermolecular interactions can lead to the ordering of a network. This was experimentally proven by Prince and Stein.

The density of a fluctuational network depends on the quality of a solvent. The probability of polymer-polymer contacts in the medium of poor solvents is much greater than in the medium of good ones. Therefore, the density of associates and of the fluctuational network in the first case is higher than in the second one. This leads to considerably higher values of the light scattering and especially viscosity of solutions, and they are always higher for solutions of a polymer in poor solvents than those in good ones (Chap. 15).

Owing to the fluctuational character of a network in a solution and its continuous change under the action of thermal motion, it is difficult to obtain the micrographs of the network in the electron microscope; this can be done considerably more easily for gels whose network is not fluctuational (see Fig. 17.3). But the network can be fixed in the former case if a solution is suddenly frozen and subjected to lyophilic drying (p. 503). That is how Vinogradov and his coworkers obtained aerogels and determined their specific surface in an ordinary way (Chap. 20). The specific surface of an aerogel obtained from a solution of PS in a good solvent turned out to be much larger than that of the specimen obtained from a solution of PS in a poor solvent.

Thus, as the concentration of a solution increases, a transition is made from isolated macromolecules to associates and to a fluctuational network, whose formation is accompanied with a sharp increase in viscosity and a decrease in light scattering. As concentration grows further, as a result of an increase in the number of contacts, the polymer-polymer network becomes denser and more ordered, the amount of the free solvent diminishes, and the entire solvent becomes bound by the polymer structures formed.

When a solvent is added to a polymer, all the above-mentioned stages of structure formation can be observed in the reverse order. When the amount of a solvent is small, inter- and intrastructural swellings occur, the structures of the polymer and of the solvent disintegrate simultaneously, and a fluctuational spatial network is formed; between the elements of this network there are thin, often monomolecular, solvate layers of the solvent that differ by their structure from a pure solvent. On further dilution (if there is absolute mixing), the polymer structure continues to disintegrate, and the groups of a polymer chain that become free of interchain interaction continue to interact with solvent molecules, forming new solvate layers. However, with any degree of dilution, one functional group of a polymer can retain not more than

1-4 molecules of a solvent, i.e., one gram of a polymer can retain 0.5-2.5 g of a solvent. It follows that, for example, 0.1 per cent solution has 0.05-0.25 g of a bound solvent per 0.1 g of a polymer, while the remaining trully dissolved or compatible solvent is "free".

One will naturally ask what will happen with macromolecular conformation as the concentration of a solution increases? Obviously, there cannot be a definite answer to this question. This depends on the nature of a polymer: on the regularity of the chain structure, its flexibility, and the crystallizability of a polymer.

The coil-helix or coil-folded conformation transition occurs as dilute solutions pass over a bulk state for crystallizing polymers in whose crystals macromolecules have helical or folded conformations (Chaps. 4 and 5).

Very flexible macromolecules of elastomer polymers in a bulk state retain the conformation of the Gaussian coil. This was shown by Flory, who scrutinized much experimental material. It is less clear what happens with non-crystallizing polymers having rigid and semi-rigid chains.

Neutron diffraction is now used to study the conformation of macromolecules in a bulk state. To increase the wavelength of neutrons, they are cooled by means of liquid hydrogen or helium. Their rate then decreases, and the wavelength λ increases to about 10 Å. Since neutrons carry no charge, they interact mainly with atomic nuclei, and not with electrons. In this case, coherent and incoherent neutron scattering may occur; this scattering proceeds quite differently for the nuclei of hydrogen and for that of deuterium. So, deuterium has considerably greater coherent scattering, while hydrogen, incoherent scattering. This difference is used in the neutron diffraction method, and polymers are deuterated for this purpose. For instance, solutions of deuterated polystyrene in a nondeuterated matrix are studied or, conversely, a nondeuterated polymer is dissolved in a deuterated matrix. A series of solutions of a deuterated polymer of different molecular mass, if possible, monodispersed polymers, is usually prepared, and they are dissolved in a protonated polymer, which serves as a diluent. Using the dependence of the intensity of scattering on the molecular mass, the dimensions of macromolecules are calculated in the same way as in the light-scattering method (Chap. 16). The results of the study of, say, polystyrene by this method have shown that macromolecules in a bulk have the same conformation as in the θ-solvent, and are described as Gaussian chains.

As Flory theoretically predicted, when the rigidity of a chain increases, there is greater probability for macromolecules to unfold with a growth in concentration, and a liquid-crystal phase may then be formed already in a solution.

17.12. LIQUID CRYSTALLINE STATE

The liquid crystalline state is such a state of a substance that, by its anisotropy, can be related to crystals and, by its mobility (fluidity), to liquids. Consequently, the liquid crystalline state is an intermediate state between solid crystals and ordinary liquids. Such substances are said to be *mesomorphous* (*mesos*, meaning "intermediate" in Greek). Organic substances, whose molecules

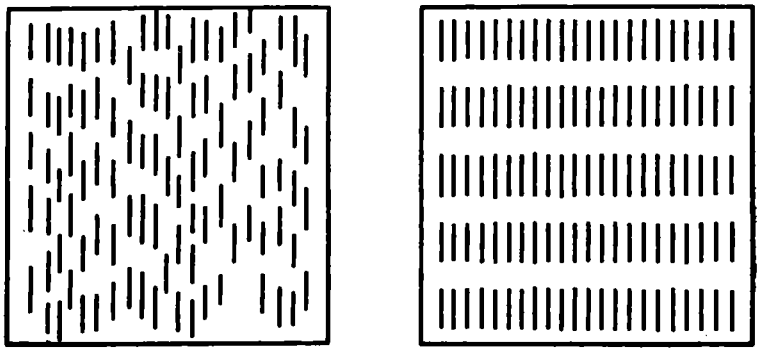
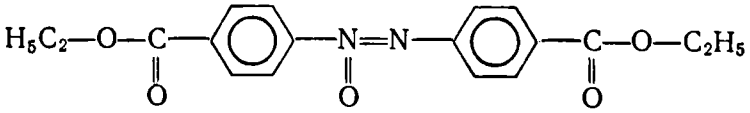


Fig. 17.8. Arrangement of molecules:
a—nematic liquid crystal; *b*—smectic liquid crystal [Chistyakov, Y. T., *Liquid Crystals*, Izd. Acad. Nauk SSSR, Moscow, 1966 (in Russian)]

have an elongated plane shape and contain polar groups which have a high dipole moment, are capable of forming liquid crystals.

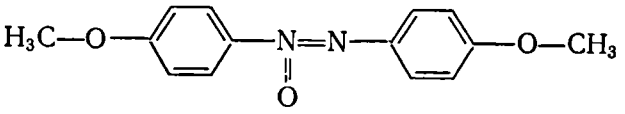
By the symmetry of liquid crystals, they are divided into three classes: smectic, nematic, and cholesteric ones.

The term *smectic* is formed from the Greek word *smegma*, meaning soap, because the structure is similar to the micellar structure of soaps. It is a laminar structure, and the orientation of molecules in each layer remains parallel (Fig. 17.8*b*). A classical example of liquid crystals of the smectic type is ethyl ester of *p*-azoxybenzoic acid:

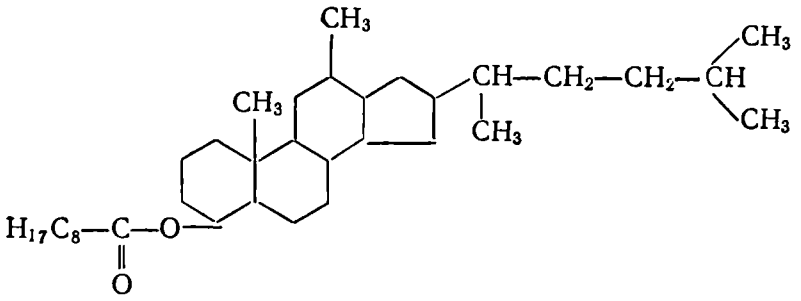


The term *nematic* is derived from the Greek word *nema*, meaning thread. Thin mobile threads are seen in the microscope in the preparations of substances which are in the nematic state. In the nematic phase, the centres of molecules are arranged randomly, as in an ordinary liquid, the axes of molecules being oriented

parallel to one another (Fig. 17.8*a*). Liquid crystals of the nematic type form *p*-azoxyanisole:



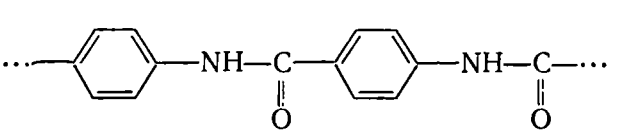
The *cholesteric* phase is similar to a nematic one, but its molecules have a twisted structure. This is characteristic of cholesterol:



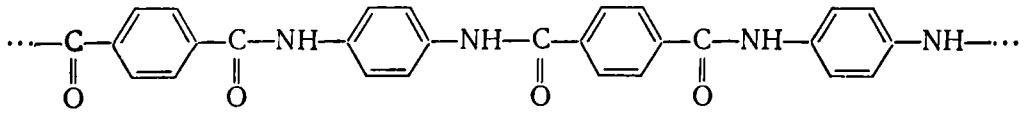
It has recently been shown that the liquid-crystal state is present in polymers. This is observed for many proteins and for some synthetic polymers.

Liquid crystals may form in solutions of:

(a) very rigid para-aromatic polymers, such as poly-*p*-benzamide:



or poly-*p*-phenyleneterephthalamide:



which are characterized by a *trans*-structure (p. 88);

(b) polymers obtained from monomers which are in a liquid-crystalline state, such as phenyl methacrylic polyesters of alkoxybenzoic acids;

(c) comb-like polymers, whose side chains contain long aliphatic substituents, which are capable of forming an interchain crystalline phase.

Papkov, Kulichikhin *et al.* have shown that the liquid-crystalline phase in a solution is formed beginning from a definite concentration, and that this is accompanied with a change in viscos-

ity, as represented in Fig. 17.9. As we have seen, such a "surge" of viscosity is very characteristic of any processes of formation of a new phase.

The liquid-crystalline order in a solution is of great importance, because the most perfect polymer crystals are formed from such

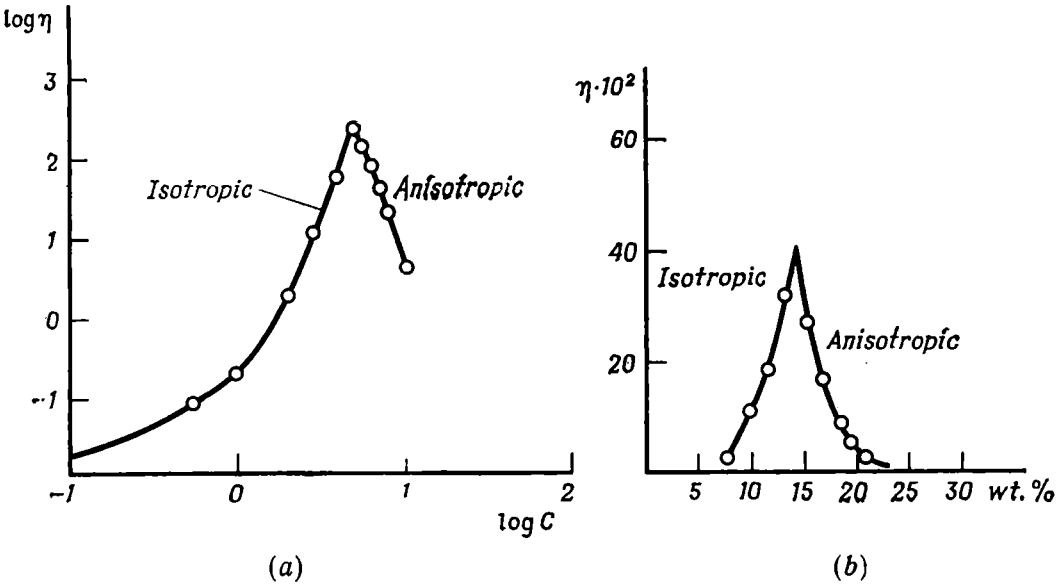


Fig. 17.9. Concentration dependence of viscosity of poly-*n*-benzamide solutions:

a — in dimethyl acetamide + 3 per cent LiCl; *b* — in HF

solutions (Chap. 5), and this is indispensable in obtaining high-strength, high-modulus fibres.

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CHAPTER 18

Plasticization

The production of polymeric materials with definite sets of properties involves not only synthesis of polymers of different chemical constitution, but also the creation of structures. One of the important methods of structural modification of polymeric materials is *plasticization.* Practically, plasticization consists in adding various liquids or solids (*plasticizers* *) to the polymer to improve its elasticity and make it frost-resistant and easier to process. Theoretically, plasticization consists essentially in altering the viscosity of the system, increasing the flexibility of its molecules and the mobility of its supermolecular structures.

Plasticizers added to a polymer affect all its physical and mechanical properties (strength, elasticity, brittleness, dielectric loss, glass-transition and flow temperatures, etc.).

18.1. EFFECT OF PLASTICIZERS ON GLASS-TRANSITION TEMPERATURE AND FLUIDITY

Many workers have studied the effect of plasticizers on the properties of polymers. However, the results of these studies are often difficult to utilize because the conclusions are based on crude investigations (e.g., measurement of the flexural fatigue life of a film). Strict scientific conclusions became possible only after methods of determining glass-transition and flow temperatures were worked out.

* Since the presence of plasticizers often improves the elastic properties of polymeric materials, they are sometimes called *elasticators.* In the rubber industry, where these substances are added to increase frost resistance of rubbers, they are known as *antifreezes.* Plasticizers added to lower the flow temperature, i.e., to facilitate processing of polymers, are often called *softeners.* There is quite evidently a lack of accuracy in current terminology.

The glass-transition temperature is a measure of frost resistance of polymeric rubber-like materials. To raise the frost resistance of polymeric materials it is necessary to lower their glass-transition temperature. The flow temperature determines the technological properties of polymers. One of the most popular methods of processing polymers is processing them in the viscofluid state. The flow temperatures of some polymers are very close to, and sometimes even above, their decomposition temperatures. Therefore lowering the flow temperature by adding a plasticizer is technologically very advantageous.

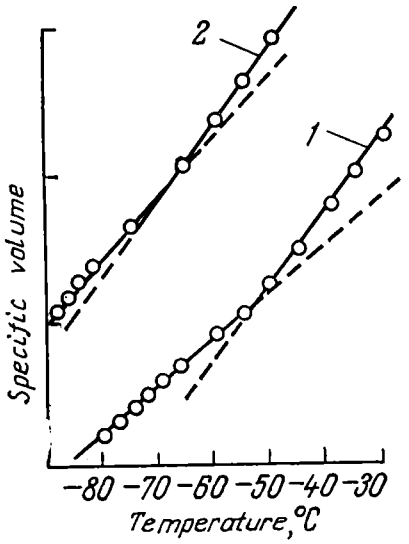

Fig. 18.1. Effect of plasticizer on glass temperature of natural rubber:
1—unplasticized sample; 2—plasticized sample

The glass and flow temperatures of plasticized systems are determined by methods which were described in Chap. 8.

The accompanying figures show the effect of plasticizers on the glass-transition temperatures of polymers obtained dilatometrically (Fig. 18.1), from deformation measurements (Figs. 18.2, 18.3), and elasticity modulus measurements (Fig. 18.4).

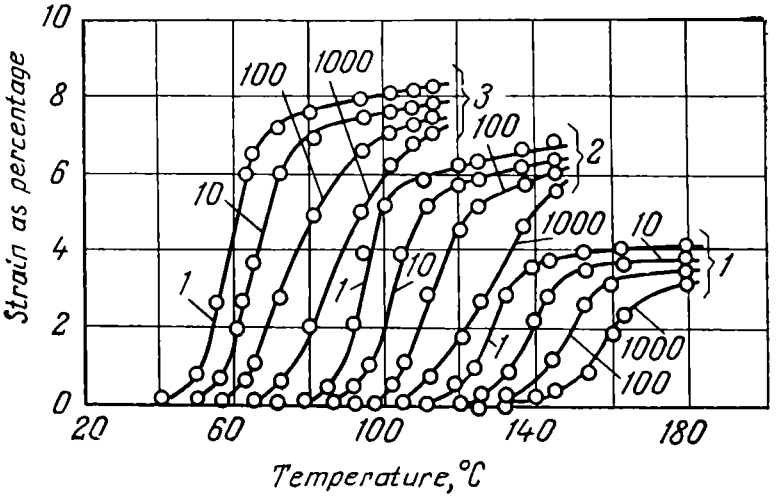

Fig. 18.2. Effect of plasticizer on glass temperature of poly(methyl methacrylate). The numbers on the curves are deformation frequencies, cps:
1—unplasticized sample; 2—10 per cent plasticizer; 3—30 per cent plasticizer

It follows from all these data that the glass-transition temperature decreases regularly with increasing plasticizer content. This

means that in the presence of plasticizers a polymer will retain highly elastic properties at lower temperatures than the unplas-

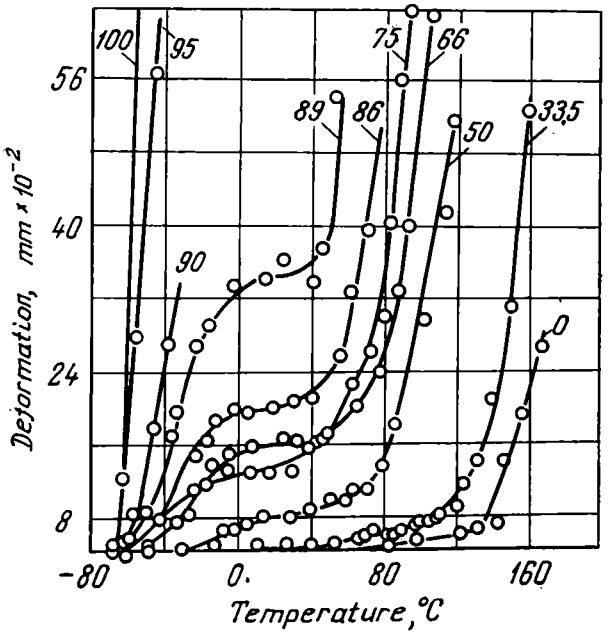

Fig. 18.3. Thermomechanical curves for plasticized poly(vinyl chloride). The numbers on the curves are percentage contents of plasticizer

ticized polymer, and that deformation and glass temperature depend on frequency of deformation. The higher the frequency, i.e., the shorter the loading time, the higher is the glass-transition temperature of the plasticized system.

The lowering of the glass-transition temperature ΔT_g is a measure of *plasticizer efficiency*. The efficiency of a plasticizer is the most pronounced in polymers with rigid chains: plasticizers depress the glass temperature of such polymers by 100-160 °C. The effect of plasticizers on flexible rubber-like polymers is much less pronounced: the glass temperature of polar rubbers can be lowered by only 30-40 °C. But if the polymer has a glass-transition temperature of, say, —90 °C, the plasticizer can lower it by only 10-20 °C.

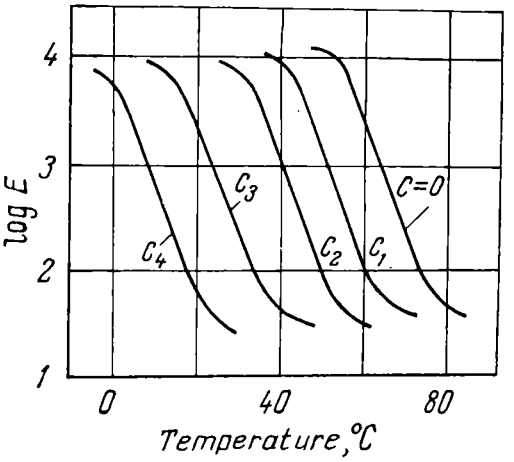

Fig. 18.4. Effect of plasticizer content on glass temperature of polymer ($c_4 > c_3 > c_2 > c_1$)

Table 18.1 lists the glass-transition temperatures of a number of plasticized polymers. These data show that the glass temperature of the polymer can be lowered very greatly by adding plasticizers. However, too much plasticizer should not be added to the polymer because this causes a sharp drop in the flow temperature and narrows the temperature range of high elasticity.

The introduction of a plasticizer causes a drop also in flow temperature. This is understandable, since the viscosity of a poly-

TABLE 18.1. *Glass-Transition Temperatures of Some Plasticized Polymers*

Poly(methyl methacrylate)-dibutyl phthalate		Poly(vinyl chloride)-dioctyl phthalate		Cellulose nitrate-dibutyl phthalate		Cellulose acetate-dimethyl phthalate	
concentration of plasticizer, wt. %	T_g	concentration of plasticizer, wt. %	T_g	concentration of plasticizer, wt. %	T_g	concentration of plasticizer, wt. %	T_g
0	110	0	81	0	Above T_{dec}	0	Above T_{dec}
	97	9.1	55	10	120	10	119
10	82	16.6	35	20	98	20	100
15	76	23	22	25	86	30	82
20	64	33.4	—8	30	76	—	—
30	51	50	—45	40	55	—	—

mer as a rule decreases when a less viscous component is introduced into it (Chap. 10), and, consequently, the system is capable of flowing at a lower temperature.

The variation of T_g and T_f with concentration of plasticizer is illustrated by Fig. 18.5. It can be seen that when the plasticizer content is low, the glass temperature decreases more sharply than the flow temperature and the difference $T_f - T_g$ increases; at higher plasticizer contents the flow temperature decreases more sharply and therefore the difference $T_f - T_g$ decreases.

In the presence of some plasticizers the difference $T_f - T_g$ remains unchanged up to a definite plasticizer concentration, after which it begins to fall off. With a certain addition of plasticizer the difference $T_f - T_g$ may become zero. This means that $T_f = T_g$, i.e., the plasticized sample does not possess high elasticity at any temperature. Its glass-transition temperature (which is the same as T_f) may be very low in this case, but above this temperature the material is not elastic but fluid.

The above reasoning suggests that the amount of plasticizer added to a polymer should be such that it does not decrease the

difference $T_f - T_g$. The usual concentrations are from 20 to 30 per cent of the mass of a polymer.

Since the presence of a plasticizer decreases the glass temperature, it lowers the heat resistance of the plastic. A plasticized material softens at a comparatively low temperature and has a narrower temperature interval of forced elasticity than unplasticized one.

If it is necessary for the polymeric material to remain solid in service, plasticizers should be avoided, or added in very limited amounts. In this way, addition of plasticizer, though convenient for the processor, may be inconvenient for the consumer.

In recent years stereoregular crystalline polymers have been synthesized (Chaps. 1 and 2) with melting points far above room temperature and with flow temperature coinciding with their melting points. Above T_m many polymers, e.g., isotactic polystyrene, pass directly into the viscofluid state. To process these polymers in the viscofluid state they have to be heated to 220 °C or more. Therefore it would be desirable to lower the flow temperature of crystalline polymers. However, investigations have shown that the addition of a plasticizer to isotactic crystalline polystyrene greatly lowers its glass temperature and has comparatively little effect on its flow temperature, which even in the presence of the plasticizer remains close to the melting point. Of great importance for obtaining correct results when studying the thermomechanical properties of plasticized polymers is sample preparation. Usually the following procedures are used:

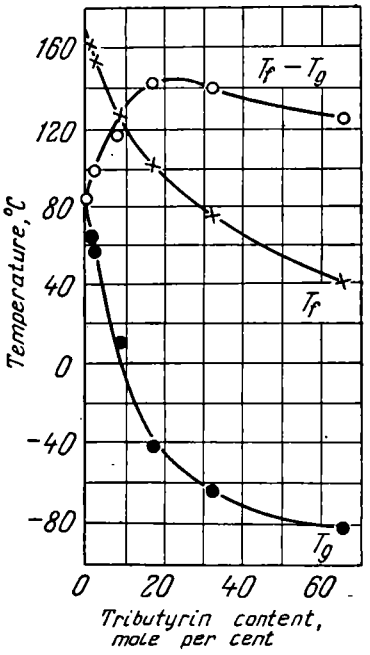

Fig. 18.5. Composition dependence of T_g, T_f, and $T_f - T_g$ for the system poly(vinyl chloride)-tributyrin

(1) The weighed polymer sample is swelled in solvent vapours. This method is suitable for volatile solvents.

(2) The weighed polymer sample is swelled in a liquid plasticizer. This method is suitable if swelling occurs at a measurable rate and there is no danger of the sample dissolving.

In both cases the concentration of plasticizer in the sample is determined by the difference of masses before and after swelling (weight per cent is recalculated to mole or volume per cent). To ensure uniform distribution of a plasticizer it is good practice to heat the plasticized sample in pre-evacuated ampoules to 100 or

200 °C (depending on the phase state of the polymer and its ability to become structurized on heating).

(3) Exactly weighed amounts of a polymer and plasticizer are mixed mechanically at room temperature and compressed into pellets in special moulds at high temperature and pressure. If the polymer is capable of structurizing at an elevated temperature, care must be taken that the moulding temperature should be below the temperature of structurization of the polymer.

18.2. EFFECT OF PLASTICIZERS ON MECHANICAL PROPERTIES

Plasticization changes all the mechanical properties of polymers substantially. Thus, the elasticity of a polymeric material, i.e., its ability to undergo large reversible deformations, is increased by the addition of a plasticizer. The same refers to forced elasticity. Hence, the addition of plasticizers is always advantageous for increasing elasticity.

Until recently it was thought that strength decreased continuously with increasing plasticizer content. However, it has been shown that the addition of small amounts of plasticizer actually increases mechanical strength. But further increase of the amount of plasticizer reduces the strength [poly(vinyl chloride), nitrile and styrene rubbers]. Thus, the dependence of strength on plasticizer concentration is extremal (Fig. 18.6).

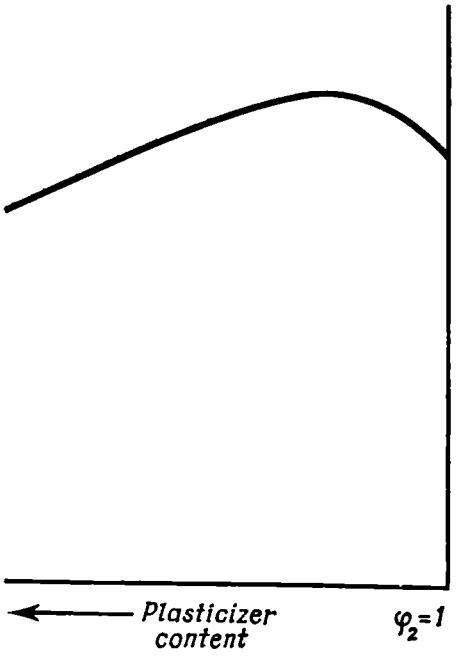

Fig. 18.6. Dependence of strength on plasticizer concentration

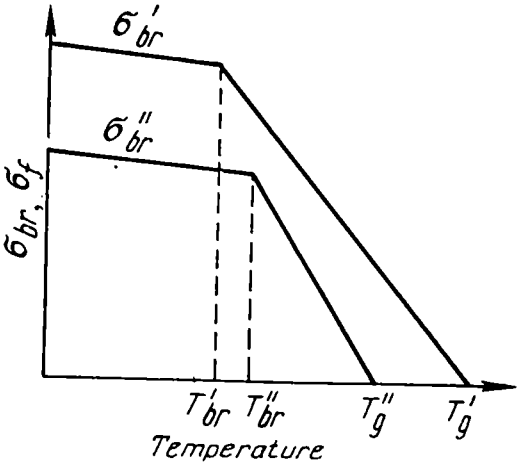

Fig. 18.7. Effect of plasticizer on brittle temperature (single primes refer to unplasticized, double primes to plasticized polymer)

The decrease in mechanical strength in the presence of a plasticizer affects the position of the brittle temperature. The addition of plasticizers lowers T_g. If σ_{br} and the slope of the σ_f vs. T curve remained unchanged, T_{br} would even decrease. However, the strength of plasticized polymers is always lower than that of unplasticized ones. Experiment shows that in the presence of a plasticizer σ_f vs. T curves become steeper and therefore the brittle temperature may even rise (Fig. 18.7). This makes the interval of forced elasticity narrower. Thus, a mixture containing 385 parts by weight of the plasticizer (phthalate) per 100 parts of poly(vinyl chloride) possesses rubber-like properties at high temperatures, whereas at low temperatures it behaves like a low-molecular brittle glass.

The brittle temperature can be lowered only by adding very large amounts of a plasticizer, i.e., at the price of a considerable decrease in heat resistance and strength at low temperatures. For this reason it is very important to synthesize new polymers with high heat resistance and low brittle temperatures.

Addition of plasticizers shortens the lifetime of polymeric materials; it does not change the activation energy of rupture, but increases the structural coefficient γ. This is due to the fact that the plasticizer molecules wedge in between the macromolecules or supermolecular structures, and that changes only intermolecular interaction.

18.3. EFFECT OF PLASTICIZERS ON DIELECTRIC PROPERTIES

The use of polymers as insulating materials is made possible by their high electrical resistance, low permittivity (dielectric constant), small dielectric loss, and resistance to high voltages (Chap. 11). The addition of plasticizers lowers all these characteristics, as a rule. For example, as a result of the decrease in viscosity of a polymer when a plasticizer is added to it, its relaxation time decreases and hence the maximum of its dielectric loss angle (power factor) shifts towards lower temperatures (Fig. 18.8). The absolute values of the loss angle and the permittivity depend on the polarity of the plasticizer, i.e., on its own permittivity. The addition of nonpolar plasticizers, which have low permittivity, reduces the ε' and tan δ_{max} of the system, but the addition of polar plasticizers may increase the permittivity and tan δ_{max} of the plasticized system.

Since the maximum of loss angle tan δ_{max} occurs at the glass temperature of the polymer, its shift is equivalent to a depression of the glass-transition temperature. Hence, the plasticizer efficiency can be assessed by the shift of tan δ_{max}: the lower the temperature corresponding to tan δ_{max}, the more efficient the plasticizer.

The dependence of T_g, determined by the maximum of dielectric loss angle, on the concentration of a plasticizer is given in Fig. 18.9. It follows from this figure that the lower the frequency at which the measurements are made, the lower will be this temperature. It follows from the given data that addition of polar plasticizers to polymeric materials used as insulators is undesirable. But sometimes it

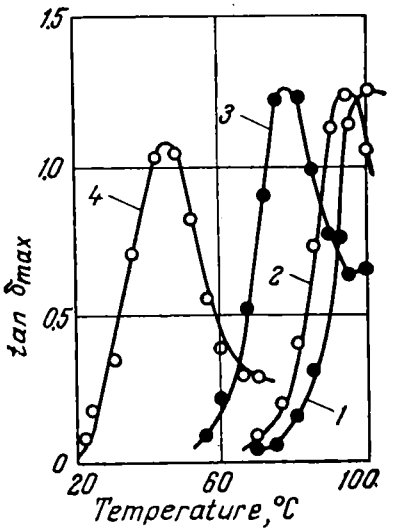

Fig. 18.8. Effect of plasticizer on tan δ of dipole-segmental losses:
1 — unplasticized poly(vinyl chloride); *2* — 1 per cent; *3* — 6 per cent; *4* — 20 per cent plasticizer

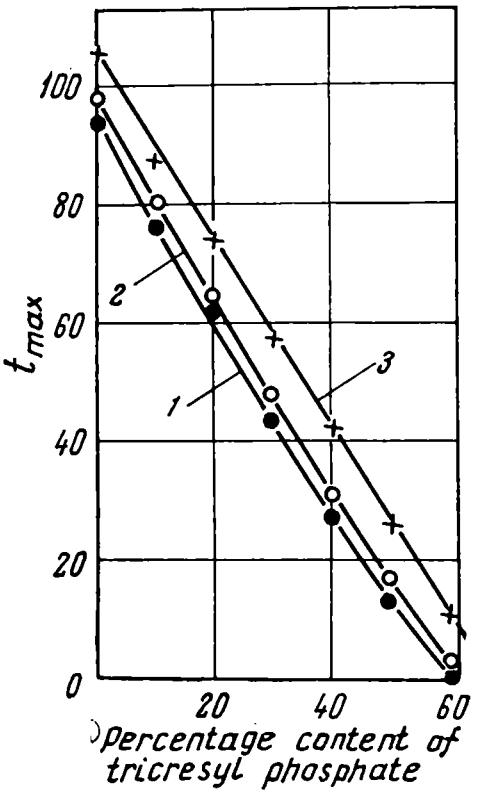

Fig. 18.9. Dependence of temperature corresponding to maximum of dipole-segmental loss t_{max} of mixtures of poly (vinyl chloride) on concentration of tricresyl phosphate:
1 — 15 cps; *2* — 260 cps; *3* — 1000 cps

is necessary to do so, because plasticizers of low polarity are poorly compatible or incompatible with polar polymers.

18.4. COMPATIBILITY OF PLASTICIZERS AND POLYMERS

Plasticizers are usually added to a polymer in the liquid state. They are, as a rule, high-boiling liquids of low volatility; the plasticizer should have a high boiling point so that it does not evaporate during processing of the polymer. Some widely used plasticizers are esters of phthalic, sebacic, phosphoric and other acids, and a number of products of natural origin (coal tar, fuel oil, and petroleum asphalt). Solids may also be used, but their softening temperature should not be too high for them to melt or soften during processing.

When a liquid plasticizer passes into the polymer phase, col-

loidal or molecular dispersion may occur (Chap. 12). If the plasticizer possesses affinity for a polymer, molecular dispersion takes place, i.e., the plasticizer spontaneously forms a true solution in polymer and the polymer swells in the plasticizer. If the plasticizer has no affinity for the polymer, it does not pass into the latter spontaneously, i.e., swelling will not occur.

Since plasticizers are added in mixers, the plasticizer may be colloidally dispersed in the polymer by mechanical energy. The resulting emulsion is a thermodynamically and aggregatively unstable system, and it separates into phases. Phase separation may occur immediately after mixing, but mostly, owing to the high viscosity of the system, phase separation occurs slowly, sometimes during storage of the article and sometimes even during its service. The outward manifestation of phase separation may be drops of the plasticizer appearing on the surface of the article. Microscopic drops of plasticizers formed in transparent articles become centres of light scattering, and the material turns cloudy.

The formation of a true solution of a plasticizer in polymer is usually termed *compatibility*. If the polymer swells spontaneously in the plasticizer, the two are compatible. Colloidal dispersion indicates incompatibility. If the polymer is incompatible with the plasticizer, the mechanical properties of the system are much worse even in the absence of the external manifestations described above. All this signifies that it is necessary to form a true solution, i.e., a thermodynamically stable polymer-plasticizer system.

It should be pointed out that there is no necessity for the plasticizer to be completely miscible with polymer. They may be partly miscible, i.e., it is enough for the polymer to swell, but not necessarily to dissolve, in the plasticizer. However, the amount of plasticizer added should correspond to its true solubility in polymer not only at the temperature of mixing, but over a wide range of temperatures as well, covering those of storage and service of the articles. If the amount of plasticizer added exceeds the concentration of a saturated solution, i.e., the compatibility limit, all the excess plasticizer will exude from the system as incompatible during processing or during storage and service. To prevent this, plasticizers should be selected according to the same rules as solvents, i.e., it is necessary to study the mixing diagrams of polymer and plasticizer and the thermodynamic affinity between them. The methods of investigating these properties were described in Chaps. 12 and 13.

Figure 18.10 is a typical coexistence curve of a polymer-plasticizer system. It is evident from the figure that all the systems studied have a UCST, and the larger the alkyl radical in the ester molecule, the higher this temperature. Lower phthalates are compatible with polystyrene over a very wide range of temperatures,

the higher ones, over a much narrower range. Below 40 °C the polystyrene-didecyl phthalate system separates into phases at any polymer content.

The plotting of polymer-plasticizer coexistence curves is no easy experimental task. For this reason in a number of cases the temperature of phase separation is determined at some concentration of the solution, i.e., one point on the coexistence curve is found. Some workers incorrectly call this temperature the critical solution temperature. The critical solution temperature is a temperature corresponding to the maximum or the minimum on a coexistence curve. If the curves are very steep, the critical solution temperature and the temperature of phase separation at a random concentration may differ very greatly.

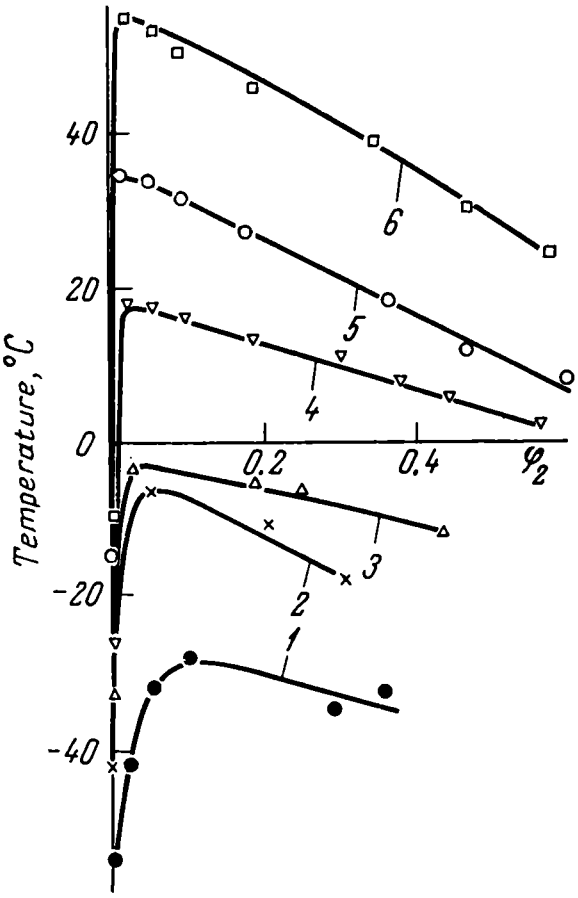

Fig. 18.10. Coexistence curves for polystyrene-phthalate systems:
1 — dimethyl ; *2* — dibutyl-; *3* — dihexyl-; *4* — dioctyl-; *5* — dinonyl-; *6* — didecyl phthalate

The phase separation of the polymer-plasticizer system can be caused also by the crystallization of the latter. In this case, there is a phase diagram, which is illustrated in Fig. 18.10 in the form of a liquidus line. The amount of a plasticizer introduced into a polymer should be such that the plasticizer would not crystallize out of the mixture in a wide temperature range, which includes the temperatures of storage and exploitation.

To estimate the thermodynamic affinity between polymer and plasticizer it is necessary to calculate $\Delta\mu_1$ or χ_1 (Chap. 13). To do so, one measures either the swelling pressure of polymer in plasticizer or the vapour pressure of plasticizer over the polymer-plasticizer system. In recent years, vapour pressures of plasticizers have been measured by the effusion method, i.e., by evaporating the vapour through very narrow openings. This method has been well developed for determining the vapour pressure of poorly volatile substances.

Plasticizers are sometimes subdivided into *solvent (primary) plasticizers* and *nonsolvent (secondary) plasticizers.* The former include substances in which a particular polymer is unlimitedly soluble, and the latter, those in which it swells limitedly. For example, castor oil is a nonsolvent plasticizer for cellulose nitrate.

A plasticizer that dissolves a given polymer poorly sometimes becomes a good solvent for it in the presence of another liquid, which itself may be either a solvent or a nonsolvent with respect to that polymer. This phenomenon is widely used in technology, two plasticizers or a plasticizer with a solvent being added to polymers instead of one plasticizer by itself.

18.5. MECHANISM OF PLASTICIZATION. ANTIPLASTICIZATION

All the polymers have a definite structure, which implies the conformation of macromolecules and their arrangement in space (Chaps. 5, 6). When a polymer is immersed in a plasticizer, the molecules of the latter, just as the molecules of a solvent, begin to penetrate into the phase of the polymer and change its structure. If a plasticizer has great affinity for the polymer (a plasticizer is a good solvent for a polymer), they infinitely mix together; in this case, the whole polymer structure gradually disintegrates in the course of dilution. The molecules of a plasticizer become implanted between macromolecules and affect the mobility of chains and units, increasing chain flexibility. Such plasticization is known as *intrastructural plasticization.* It is characterized by a continuous drop in the glass-transition temperature T_g as an increasing amount of the plasticizer is introduced (curve *1*, Fig. 18.11*a*). If the plasticizer is a poor solvent of a polymer and mixes with it only to a limited extent, its molecules destroy some structures, while other structures remain undestroyed. Such plasticization is known as *interstructural plasticization.* It is characterized by a drop in T_g to a definite value; a further introduction of the plasticizer does not affect the position of T_g (curve *2*, Fig. 18.11*a*). In this case, when a small amount of the plasticizer is introduced, the drop in T_g can be expressed more strongly than in the case of intrastructural plasticization.

The maximum concentration of a plasticizer that produces plasticizing action corresponds to its compatibility limit, i.e., to the amount of a plasticizer truly dissolved in a polymer. This amount corresponds to the binodal points of the polymer-plasticizer systems, and this is clearly seen by comparing Figs. 18.11*a* and *b*. If the polymer-plasticizer system has a low UCST, a continuous drop in T_g to the glass temperature of the plasticizer is observed

in the entire temperature range above the binodal. If UCST is in the high temperature range, T_g drops to temperatures which correspond to binodal points at a given value of the volume fraction of a polymer in the system. Hence, in interstructural plasticization, the action of a plasticizer (drop in T_g) is the greater, the worse is a solvent thermodynamically.

Interstructural plasticization was first discovered by Kargin and Kozlov; it has much in common with antiplasticization, which

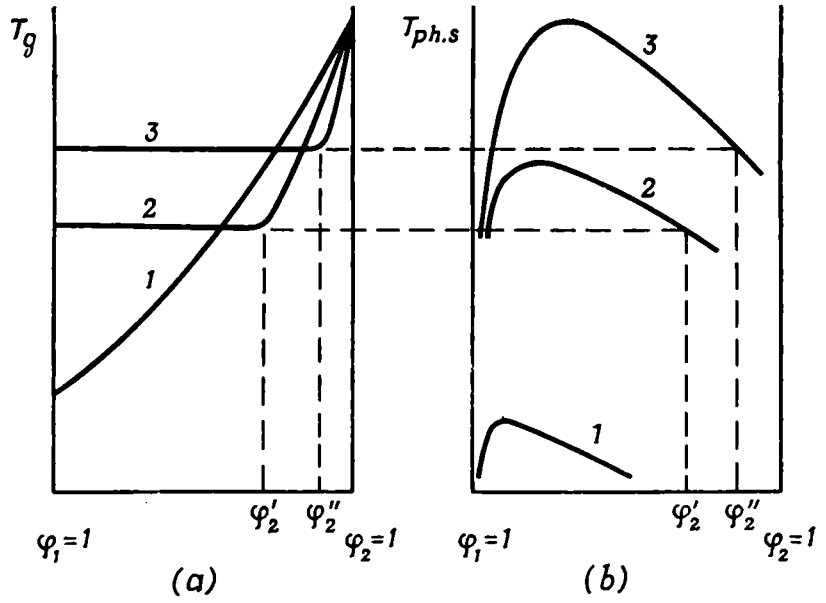

Fig. 18.11. *a* — change in T_g at intrastructural (*1*) and interstructural (*2*, *3*) plasticization; *b* — binodals of polymer-plasticizer system

was discovered by Jackson and Caldwell, who showed that when some substances are introduced into polycarbonate based on bisphenol A, the elasticity modulus and tensile stress grow, while relative elongation diminishes. Since it was believed earlier that these parameters change oppositely on plasticization, they called this phenomenon *antiplasticization.*

But it should be noted that a growth in strength and a diminution in relative elongation when comparatively small amounts of a plasticizer are added occur also in other polymers (Fig. 18.6). Hence, antiplasticization is a quite common phenomenon observed more often in respect of rigid-chain polymers that are in a glassy state, but it takes place also for rubbers prepared on the basis of some natural rubbers. The mechanism of this process is connected with interstructural plasticization at which plasticizer molecules are physically adsorbed at the interfaces of structures that exist in polymers. Physical adsorption always occurs in glassy polymers, many of which have a developed porous structure (p. 605).

But how it occurs in natural rubbers is less understandable. Physical adsorption is a thermodynamically necessary process which is accompanied with a reduction in free energy, i.e., it is a spontaneous process. In this case, the plasticizer acts as a surface-active substance, which forms adsorption layers. The greater the length of the hydrocarbon radical in the plasticizer molecule and the lower its solubility in the polar polymer, the better is it adsorbed and the more sharply does T_g drop. In this case, there is a regularity characteristic of a boundary lubricantion (lubricant formed by the monomolecular layer of the adsorbed molecules), i.e., the higher the viscosity of a substance, the greater is its lubricating action. Indeed, in the low concentration range of a plasticizer, the higher the viscosity of the plasticizer, the greater is the drop in T_g.

Hence, the mechanism of intrastructural plasticization consists in the action of a plasticizer on the flexibility of macromolecules; this flexibility increases, and therefore the elasticity range is maintained to low temperatures. The mechanism of interstructural plasticization (and antiplasticization) consists in the fact that the adsorption layers formed play the part of a boundary lubricant, facilitating mutual displacement of supermolecular structures, and the more flexible the plasticizer molecules, the more intensive this displacement. In a number of cases increased mobility of structural formations favours their mutual orientation, which always increases mechanical strength. That is why small plasticizer additions increase rather than reduce the strength of some polymers. This may play a positive role for amorphous polymers. In the case of crystalline polymers the increased mobility of structures resulting from interstructural plasticization may sharply accelerate recrystallization and cause brittleness. This is observed very often when crystalline polymers are plasticized.

18.6. THEORY OF PLASTICIZATION

The first attempt at a theoretical examination of plasticization was made by S. Zhurkov, who related this process to the mechanism of glass transition of polymers (p. 209). He supposed that the glass-transition temperature of a polar polymer is determined by the interaction of polar groups of neighbouring chains. The plasticizer for such a polymer is a polar liquid. The polar groups of the polymer are solvated by the polar groups of the plasticizer, each polar group of the chain strongly binding one or two plasticizer molecules (Chap. 12). Shielded by the plasticizer molecules, the polar groups of neighbouring chains cannot interact with each other; the number of free polar groups in the polymer chain becomes smaller, and hence, in accordance with the glass-transition

mechanism described in Chap. 8, the polymer passes into the glassy state, or hardens, at a lower temperature.

If the plasticizer molecules do not differ very greatly in size and have different polar groups $\left(-OH,\ -COOH,\ \diagdown\!\!\diagup CO,\ \text{etc.}\right)$, each of which can solvate one polar group of the polymer chain, the number of groups eliminating from interaction will obviously be the same. Then the depression of the glass temperature ΔT_g should be proportional to the number of moles (mole per cent) of plasticizer added:

$$\Delta T_g = kn \tag{18.1}$$

where k = proportionality coefficient
n = number of moles of plasticizer.

Equation (18.1) is often called *Zhurkov's rule* or the *rule of mole concentrations.*

Experimental data, some of which is described below (p. 564), shows that Eq. (18.1) is not always valid. With the same polar groups in the plasticizer molecule the change in glass-transition temperature of a polymer depends on the size and shape of the plasticizer molecule, and this dependence is still more pronounced upon plasticization of nonpolar polymers with nonpolar plasticizers. For example, with equal numbers of carbon atoms in the molecule linear molecules (e.g., *n*-hexane) shift the glass temperature of polyisobutylene more strongly than cyclic molecules (e.g., cyclohexane or benzene).

Kargin and Malinsky suggested the following equation for the plasticization of low-polar and nonpolar polymers:

$$\Delta T_g = k\varphi_1 \tag{18.2}$$

where φ_1 is the volume fraction of plasticizer.

This equation has become known as the *rule of volume concentrations.* According to the authors' opinion, the most important factor in this case is not the energy of polymer-plasticizer interaction, but the conformational changes of polymer chains in the solution accompanied by a change of entropy (Chap. 13). In solutions in different solvents which occupy equal volume fractions, the number of conformations the polymer chains can acquire should always be the same. Hence, an equal volume fraction of solvent or plasticizer may be expected to cause an equal shift of T_g. Therefore the depression of the glass-transition temperature should be proportional to the volume fraction of plasticizer φ_1.

Equation (18.2) is not valid even for all nonpolar systems, but it quite correctly directs attention to the fact that the effectivity of plasticizers should be closely related to their specific volume, which, as was indicated above, depends on free volume,

The idea of free volume lies at the basis of all subsequent theories of plasticization.

Bueche and Kelley consider that the free volume of a solution is the additive sum of the free volumes of its components, and hence the relative free volume of solution f can be expressed through the relative free volumes of polymer f_p and solvent f_s as follows:

$$f = \frac{V_f}{V} = f_p\varphi_2 + f_s\varphi_1 \tag{18.3}$$

where φ_2 and φ_1 are the volume fractions of polymer and solvent (plasticizer).

Expressing f through the coefficients of thermal expansion [Eq. (8.1), Chap 8], they obtained the equation

$$f = [0.025 + \alpha_p(T - T_{g,p})]\varphi_2 + [0.025 + \alpha_s(T - T_{g,s})]\varphi_1 \tag{18.4}$$

where $T_{g,p}$ and $T_{g,s}$ = glass-transition temperatures of polymer and solvent

α_p and α_s = their coefficients of thermal expansion.

At the glass-transition temperature ($T = T_g$) the relative free volume of a plasticized system $f = 0.025$. Substituting this value into Eq. (18.4) we get an expression for the glass-transition temperature of a plasticized system:

$$T_g = \frac{\alpha_p\varphi_2 T_{g,p} + \alpha_s(1 - \varphi_2)T_{g,s}}{\alpha_p\varphi_2 + \alpha_s(1 - \varphi_2)} \tag{18.5}$$

Equation (18.5) relates the glass temperature of the system to the glass temperatures of the components, but it contains no terms allowing for the interaction between them. This leads to incorrect results. For example, according to Eq. (18.5), if two polymers with equal T_g [e.g., polystyrene and poly(methyl methacrylate)] are plasticized with the same plasticizer, the T_g of the plasticized system should also be the same, but this is not confirmed by experiment.

Interaction between plasticizer and polymer is taken into account by the Kanig theory, also based on the free volume concepts. According to this theory, a polymer melt is regarded as a liquid saturated in vacant sites, and a plasticized polymer, as a three-component solution consisting of a polymer, a plasticizer, and vacancies. Only dispersional interaction is taken into account, i.e., the mutual orientation of the molecules is considered to be of no consequence. The energy of intermolecular interaction is calculated on the assumption that in first approximation the interaction is proportional to the area of contact between the molecules. The configurational entropy ΔS_{conf} is calculated from Eq. (14.23) of Chap. 14 and the thermodynamic affinity between all species of

molecules ($A_{p,p}$ between polymer molecules, $A_{w,w}$ between plasticizer molecules, $A_{p,w}$ between polymer and plasticizer molecules), from Eq. (14.27) of the same chapter. As a result, the equation for the glass-transition temperature lowering ΔT_g becomes

$$\Delta T_g = T_{g,p} - T_g = k_1 \frac{T_g}{V_{f,w}} + k_2 (A_{p,p} - A_{p,w}) + k_3 (A_{p,p} - A_{w,w}) \tag{18.6}$$

where T_g and $T_{g,p}$ = glass temperatures of plasticized system and of polymer
$V_{f,w}$ = free volume of plasticizer
k_1, k_2 and k_3 = quantities depending in a complicated way on the composition of solution and the free volumes of the components.

Calculation of k_1, k_2, and k_3 encounters great difficulties, and for this reason Eq. (18.6) cannot be used as yet for calculating ΔT_g, but qualitatively it discloses a number of very important regularities.

1. If the affinity between all components is equal,

$$A_{p,p} = A_{w,w} = A_{p,w} \tag{18.7}$$

the second and third terms of Eq. (18.6) vanish and the plasticizer efficiency depends only on the free volume of a plasticizer. In this case Eq. (18.6) can be simplified to the following form:

$$T_g = \frac{T_{g,p}}{\frac{k_1}{V_{f,w}} + 1} \tag{18.8}$$

According to Eq. (18.8), the greater the value of $V_{f,w}$, the smaller will be the denominator of the fraction and the higher will be the T_g of the plasticized system, i.e., the smaller will be ΔT_g.

Kanig suggests that the free volume $V_{f,w}$ increases with increasing size of a plasticizer molecule.

Hence, theory predicts a decrease of plasticizer efficiency with increasing molecular mass of a plasticizer.

2. If the affinity between components is not equal, i.e.,

$$A_{p,p} \neq A_{w,w} \neq A_{p,w} \tag{18.9}$$

and $A_{p,p} > A_{w,w}$, then according to Eq. (18.6), with plasticizer molecules of equal size ($V_{f,w} = \text{const}$), the greater the differences $A_{p,p} - A_{w,w}$ and $A_{p,p} - A_{p,w}$, i.e., the more pronounced the difference of affinities between polymer and plasticizer molecules, the greater should be the glass temperature lowering. In other words, theory predicts that a compound which dissolves a parti-

cular polymer poorly, i.e., is poorly compatible with it, should be a good plasticizer capable of causing the greatest glass temperature lowering. This case was discussed on p. 557.

Kanig's theory is of great interest, but, like other theories, it is based on a number of simplifying assumptions; it overestimates the role of free volume and makes no allowance for configuration and conformation of plasticizer molecules.

The free volume of a liquid is a very important characteristic of the latter. But the ratio of free to occupied volume is also essential. Thus, the specific volume of esters (phthalates, sebacinates, etc.) grows with increasing molecular mass (size of alkyl radical), but this is due mainly to increase of occupied volume. With increasing degree of polymerization free volume should decrease.

The configuration and conformation of the plasticizer molecules have a very strong effect on the glass temperature of the plasticized system. This was first shown quantitatively by Gibbs and Di Marzio, who demonstrated that, other conditions being equal, plasticizers with flexible molecules capable of assuming various conformations are much more effective. Within homologous series of plasticizers, where molecular flexibility is constant, plasticizer efficiency decreases with increasing molecular mass.

Thus, theory predicts that glass temperature lowering depends on the chemical nature of a plasticizer.

18.7. EFFECT OF CHEMICAL CONSTITUTION, SIZE, AND SHAPE OF PLASTICIZER MOLECULES ON PLASTICIZER EFFICIENCY

In the early studies devoted to plasticization insufficient attention was paid to the chemical nature of plasticizers. It was thought that the main factor was the number of molecules of the plasticizer added or the volume it occupied in the system. However, both the rule of mole concentrations and that of volume concentrations are limiting ones, and in real systems the two principles overlap. Nowadays both theory and experiment confirm that the chemical nature of plasticizers as well as the size and shape of their molecules are major factors of plasticizing effect and of compatibility with polymers.

The effect of size of plasticizer molecules "in the pure form" can be demonstrated, for example, by *self-plasticization*, i.e., plasticization of a polymer with its low-molecular analogues — hydrogenated dimers, trimers, etc. In these cases Eq. (18.7) is observed and the T_g of the system increases with molecular mass of a plasticizer.

Indeed, it was shown in a study of self-plasticization of polystyrene that increasing the molecular mass of either a plasticizer

or a polymer raises the glass temperature until it reaches a certain constant value. Hence, increasing the molecular mass of a plasticizer in itself can only lower plasticizer efficiency. For this reason, from the point of view of glass temperature lowering, plasticization of a polymer with a polymer, which will be discussed below, is always less effective than plasticization with low-molecular substances. Other conditions being equal, the best plasticizers should be compounds with the lowest molecular mass which, however, ensure sufficiently high boiling points (250-300 °C). The advantage of self-plasticization is that, having the same chemical structure, plasticizer and polymer are readily compatible. The situation is different if compounds differing in chemical constitution from the polymers are used as plasticizers. For example, increasing the size of the alkyl radical in a homologous series of esters, on the one hand, enhancés the flexibility of the plasticizer molecule, and, on the other, reduces interaction with polymers of low affinity for saturated hydrocarbons [e.g., poly(vinyl chloride), poly(methyl methacrylate), polystyrene, and cellulose acetates and nitrates]. Hence, with increasing size of alkyl radical the compatibility of plasticizers with the polymers indicated should become worse, this being manifested in a regular rise of UCST (see Fig. 18.10). This means that increasing the molecular mass of a plasticizer increases the differences $(A_{p,p} - A_{w,w})$ and $(A_{p,p} - A_{p,w})$.

Thus, with increasing size of plasticizer molecule the first term in Eq. (18.6) decreases while the other two increase. As a result, ΔT_g should vary, depending on the size of the alkyl radical in the ester molecule, along a curve with a minimum. This has repeatedly been observed in experiment (Fig. 18.12).

The position of the minimum on the T_g vs. n_{CH_2} curve depends on the nature of polymer and plasticizer, as well as on the concentration of the latter. Thus, in a system containing 30 vol. per cent of plasticizer (the most common ratio), the minimum on the curve corresponds to dibutyl phthalate, and in a system containing 17 vol. per cent of a plasticizer, to dioctyl phthalate. When the plasticizer content is small (interstructural plasticization), the minimum on the curve should shift sharply to the right, i.e., should correspond to an ester with a larger alkyl radical.

It follows from these data that reducing the affinity of a plasticizer for a polymer favours lowering of T_g, but only up to a certain limit, where the size of the plasticizer molecule begins to make itself felt.

The effect of flexibility of plasticizer molecules, i.e., their internal mobility, can be brought out vividly by comparing the plasticizing effect of esters of different dicarboxylic acids. In this case it is more correct to compare T_g at equal molar volumes than

at equal n_{CH_2} values in the alkyl radical. Esters of naphthalic acids are worse plasticizers due to the high rigidity of their molecules caused by the presence of condensed nuclei. With increasing internal mobility the plasticizing effect of plasticizer molecules improves. The presence of condensed nuclei in the plasticizer molecule and increasing the number of aromatic nuclei it contains, e.g., passing from diphenyl to naphthalene and anthracene, lowers plasticizer efficiency. Anthracene and its derivatives are poor plasticizers for poly(vinyl chloride).

The compatibility of a polymer with a plasticizer also depends on the chemical constitution of the latter's molecules. Since the polymer need not necessarily be completely miscible with the plasticizer, the rule "like swells in like" is approximately valid here. Thus, various high-boiling hydrocarbons or esters with fairly large alkyl radicals are usually used for plasticizing nonpolar polymers. Strongly polar plasticizers cannot be used in these cases owing to their poor compatibility with a polymer.

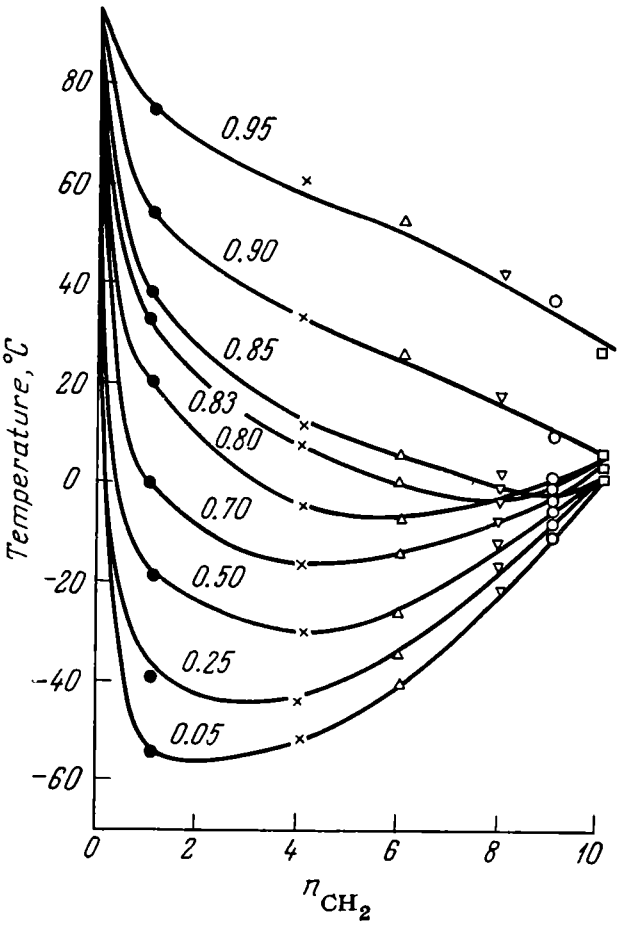

Fig. 18.12 Dependence of T_g on length of alkyl radical in PS-phthalate systems. The numbers on the curves are molar fractions (N_2) of PS in system.

Polar polymers are plasticized with such substances as glycerine. Esters are used for plasticizing poly(vinyl chloride), but hydrocarbons are not.

However, there is no full correlation between the efficiency of a plasticizer, its compatibility with polymer and the polarity of its molecules. This is due, first of all, to the fact that at present no methods are practically available for evaluating the polarity of molecules effectively. Secondly, the polarity of molecules affects only their energy or heat of interaction, whereas compatibility is due to thermodynamic affinity, which depends both on heat of

mixing, and on entropy of mixing (Chap. 13). Strong energy interactions between components always result in negative entropies of mixing, which does not favour complete miscibility. For this reason it is very important to increase the combinatorial part of the entropy of mixing, which is possible if the plasticizer molecules are very flexible. Other conditions being equal, plasticizers whose molecules possess internal mobility are always more compatible with a polymer.

Of great significance is the molecular mass of a plasticizer. Substances with large molecules themselves have high glass temperatures, and besides, it is very difficult for large molecules to penetrate between especially closely packed polymer molecules. For example, Tinius points out that plasticizers with molecules 25 Å long are already unable to penetrate between the molecules of poly(vinyl chloride). In this case the shape of the plasticizer molecules and their capacity for conformational transformations play a very important part. As a rule, elongated molecules are better as plasticizers and are more compatible with polymers than tight, spherical molecules.

Thus, we can now set out some of the requirements a plasticizer should meet.

Plasticizer molecules should be of optimum size ensuring penetration between the polymer molecules and maximum depression of T_g, on the one hand, and have a sufficiently high boiling point, on the other. They should be as elongated as possible in shape and possess internal mobility, i.e., ability to undergo conformational changes, and should be compatible with the polymer, but need not necessarily dissolve it completely. The compatibility limit should be such as to preserve thermodynamic stability of the plasticized system over a wide range of temperatures, covering the temperatures of processing, storage and service. A plasticizer should have a tendency to supercool, since crystallization of the plasticizer on to the surface of articles always greatly lowers their quality.

To ensure incorporation in the polymer, and mainly to reduce the viscosity of the plasticized system, which is very important (Chap. 15), the viscosity of the plasticizer should be as low as possible. To effect a considerable depression of the glass temperature, use should be made of plasticizers which are readily compatible with polymers. If it is necessary to lower the glass temperature not very much, and the addition of large amounts of plasticizer has an adverse effect on the other properties of the polymeric material, plasticizers should be used which are poorly compatible with the polymer in question, and they should be added in very small quantities.

Other requirements for plasticizers (resistance to extraction by water, oils, or by any other medium) depend on the conditions under which the finished articles are to be used.

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CHAPTER 19

Polymer Mixtures

Notwithstanding the large number of new synthesized polymers, mixtures of two or more polymers are now being increasingly used in industry as raw material for preparing various articles. The production of such mixtures makes it possible to improve the properties of individual polymers, e.g., to increase rubbers' strength by adding stronger plastics to them or to improve the elastic properties of plastics by adding rubbers to them. In the latter case, rubbers act as high-molecular plasticizers.

To obtain the necessary set of valuable properties, polymers which differ from one another by their properties and chemical structure are usually mixed together, mostly in different mixers. Inhomogeneous mixtures which readily laminate in scales are often obtained; the mechanical properties of such mixtures are worse than that of individual polymers. The term "incompatibility" of polymers was coined for such cases. Conversely, the term "compatibility" was used for homogeneous mixtures having good mechanical properties.

The term compatibility is used for the polymer-plasticizer system (Chap. 18). It reflects the mutual solubility of components and the formation of a true solution out of them. Similarly, thermodynamic compatibility of two polymers implies the formation of a true solution of one polymer in another one. However, it is difficult to estimate the mutual solubility of two solid polymers. Therefore, at first the compatibility of polymers was estimated in solution.

19.1. COMPATIBILITY OF POLYMERS IN SOLUTION

Dobry and Boyer-Kawenoki proposed the method of estimating the compatibility of polymers by the behaviour of their solutions.

To this end, clear solutions of two polymers in the same solvent are poured together. If the solution remains clear, it is assumed that the polymers are compatible, and if the solution becomes cloudy and separates into two layers, each of which contains mainly one of the polymers, it is assumed that the polymers are incompatible. Solutions are separated into phases not at all polymer concentrations. For example, dilute solutions do not separate at all. Separation practically does not occur in highly concentrated solutions owing to their very high viscosity. Therefore, an average concentration range is selected, say 5-10 per cent, so that the formation of two layers will not take too much time.

Dobry and Boyer-Kawenoki used this method to study 78 pairs of polymers and discovered that only three of them were compatible in solution: cellulose nitrate (CN)-poly(vinyl acetate), CN-poly(methyl methacrylate) (PMMA) and cellulose benzoate-polystyrene (PS). Kern and Slocombe investigated another 30 pairs of polymers and showed that even polymers which are similar to one another by their chemical structure (PS and polyparachlorostyrene) separate in solutions. Other investigators have also shown that most polymer pairs separate in solution. The conclusion was then drawn that polymer compatibility is an exception, while incompatibility is a rule.

19.2. DETERMINATION OF MUTUAL SOLUBILITY OF POLYMERS

The mutual solubility of polymers in the condensed state is determined by measuring the optical density of films obtained from solutions of two polymers in a common solvent after the latter is evaporated. If the polymers are mutually soluble, the films are clear, and if they are insoluble, particles of the second phase, being light-scattering centres, are formed in them. Usually, films are prepared that contain different amounts of polymers. An addition of small quantities of the second polymer does not change optical density; when the amount of the second polymer is so great that it does not dissolve any longer, the film becomes cloudy, and a discontinuity appears on the curve of dependence of optical density on the concentration of the second component (Fig. 19.1). The concentration at which this is observed is known as the limit of solubility of a polymer in another one. Kuleznev and coworkers have shown by this method that the solubility of PS in PMMA is 0.9 per cent by weight, PMMA in PS is 1.9 per cent, and PS in polyisoprene (PIP) is 1.8 per cent. It was also ascertained that the solubility of a polymer in another one depends on its molecular mass. Extrapolating this curve, Kuleznev drew the conclusion that PS, whose molecular mass is 500 and 1600, is infinitely soluble in PIP and PMMA, respectively. Radbil, Razinskaya and

Shtarkman showed by this method that poly(ethyl acrylate) and poly(butyl acrylate), which have a molecular mass of about 2000, are insoluble in PMMA. These data indicate the negligibly small mutual solubility of most polymers. At the same time, the determination of the optical density of films of a mixture of poly(vinyl acetate) (PVA) and CN has shown that they are clear in all proportions of components, i.e., these polymers are mutually soluble.

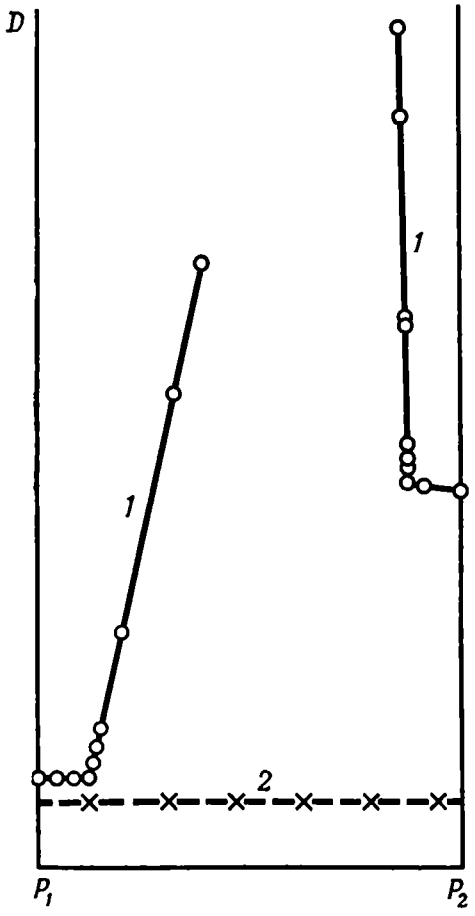

Fig. 19.1. Change in optical density D of the films of polymer mixtures when one of the components is added to the other

It follows from these data that mutually soluble polymers form true solutions, while mutually insoluble ones form two-phase colloidal systems when they are forcibly mixed; this is confirmed when they are studied by direct structural methods.

19.3. STRUCTURE OF POLYMER MIXTURES

The first structural investigations of polymer mixtures were performed by the electronographic method by Karpov and Rylov. They studied mixtures of polyisobutylene (PI) and natural rubber, polyethylene (PE) and PI, and natural rubber and gutta-percha. For all systems, electron diffraction pattern showed reflexes characteristic of individual polymers, indicating that the components of a mixture crystallize independently of one another. Slonimsky and coworkers have shown that the X-ray pattern of mixtures of a series of polymers are a superposition of patterns observed for individual components. These data indicate the absence of polymer compatibility. Galperin, Konkin and others have shown that crystalline polymers are compatible only when they are isomorphous and capable of crystallizing in the same crystallographic lattice. These authors have calculated that for crystalline polymers to be compatible, the difference in their structural parameters should not be more than 0.2-0.3 Å.

The methods of optical and electron microscopy are now widely used for studying the structure of polymer mixtures. Fig. 19.2*a* gives a micrograph which is typical of polymer mixtures. It shows a two-phase system which suggests a colloidal solid-solid system.

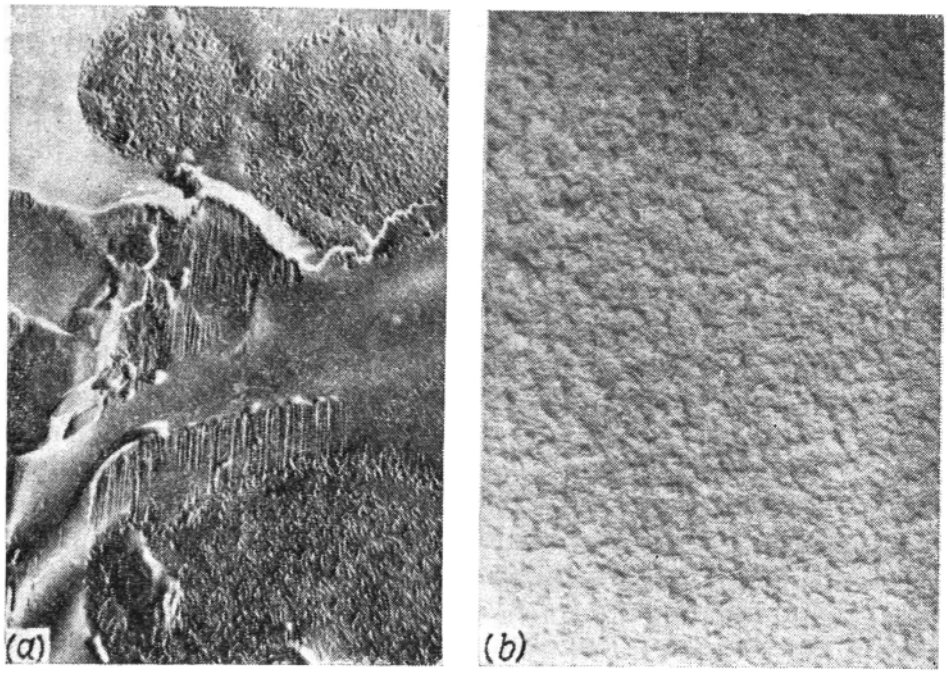

Fig. 19.2. Micrograph of two-phase (*a*) and one-phase (*b*) polymer system

Such a picture is observed for most polymeric systems; only a very few mixtures, formed from mutually soluble polymers, do not produce a two-phase system (Fig. 19.2*b*).

19.4. MODERN CONCEPTS OF THE STRUCTURE OF TWO-PHASE COLLOIDAL POLYMER-POLYMER SYSTEMS

Since most polymers are mutually insoluble and form two-phase colloidal systems, their structure should consequently be considered in greater detail, because it is precisely such systems which are dealt with in practice.

Thermodynamically, colloidal systems are unstable. They tend to the minimum of free energy, and this is usually accompanied with an increase in their degree of dispersion, i.e., with the merging of drops or the aggregation of solid particles. For a colloidal system to be stable, it is necessary to prevent this aggregation, and this is attained by introducing stabilizers, i.e., substances which are adsorbed at the particle-medium interface. In addition, the viscosity of the medium is very important. If suspended par-

ticles of even quite large dimensions are in a very viscous medium, their mobility is hindered, and their aggregation becomes practically impossible.

Experiments show that two-phase solid polymer mixtures often exist for an infinitely long time. What are the factors determining their stability?

According to modern concepts, the stability of colloidal polymer-polymer systems is determined by three factors:

1. High macroviscosity of the system.
2. Low surface tension at the interface of two polymers.
3. Presence of transition layers.

Polymer macroviscosity is very high even in melts (Chap. 10), while in the solid state it attains values of $\sim 10^{14}$ poises. Therefore, if a definite degree of polymer dispersion can be forcibly attained on rollers or in mixers, apparently it should not change in the solid state. But obtaining this adequate degree of dispersion is determined by the possibility of the formation of transition layers.

The concepts of transition layers arose when polymer adhesion was being studied. *Adhesion* is linkage between nonuniform contacting surfaces that causes solids to cement to one another; one of the solids is known as the *substratum*, and the other, as the *adhesive*. This phenomenon is very important in the production of various constructions involving two polymers, a polymer and a metal, or a polymer and a filler. Adhesion is essential for polymer coatings, which must have a strong adhesive link with the surface on which they are coated, and so forth. When the nature of surfaces is the same, we speak of *autoadhesion*. There are different theories of adhesion, but not a single one of them describes it well enough due to the complexity of the phenomenon.

According to the theory elaborated by S. S. Voyutsky, two polymers interdiffuse at their interface, as can be easily imagined for mutually soluble polymers. If polymers are limitedly soluble, isolated chain segments diffuse, as a result of which a transition layer is formed at the interface that consists of various types of segments. The presence of transition layers has been detected by the methods of light and electron microscopy. Their thickness may be as much as several thousand angstroms. Segmental diffusion is confirmed by determination of polymer-polymer diffusion coefficients.

Concepts of segmental diffusion and the transition layers, proposed to explain the formation of adhesive linkage, were applied also to the processes of polymer mixing. It was assumed that even incompatible polymers locally interdiffuse.

These concepts were used to calculate the possible thickness of the transition layers formed in polymer mixing. For example, if

the particle diameter is 1 when the interface surface is $6 \times \times 10^4$ cm²/g and the thickness of the transition layer is 1000 Å, the transition layer in a mixture of 2 g of polymers contains 0.6 g. Consequently, about 30 per cent of polymers are in transition layers. These data conform with those on the solubility of oligomers in polymers (p. 569) and indicate that segments mutually dissolve in two-phase systems at their interface even when polymers are not mutually soluble. The transition layer, which is quite thick, acts as a stabilizer that ensures the stability of a two-phase system.

19.5. MECHANICAL PROPERTIES OF POLYMER MIXTURES

As we have already seen, polymeric materials are widely used in industry largely owing to their valuable mechanical properties. The first works on mechanical properties of polymer mixtures were those by Voyutsky, Alexeyenko and coworkers, and by Slonimsky and coworkers. The authors investigated the mechanical properties of mixtures of poly(vinyl chloride) (PVC) and cellulose nitrate (CN) with butadiene nitrile rubbers. Figure 19.3 shows that mixtures have satisfactory mechanical properties when the content of polar groups in rubber is high. As the content of nitrile groups diminishes, tensile strength sharply decreases and elastic properties worsen. This is also true of mixtures of CN and the same rubbers.

Slonimsky and coworkers studied the mechanical properties of rubbers on the basis of mixtures of several pairs of rubbers. The authors drew attention to the fact that extremum dependence of properties on the composition of a mixture is observed for rubbers prepared by combining styrene rubber СКС-30 and butadiene rubber СКБ, and nitrile rubber СКН-18-СКБ, and they connected this with the inhomogeneity of the mixtures obtained. Such anomalies were not observed in mixtures of rubbers which are closer by their chemical structure: СКБ and НК, and НК-СКС-10, although these rubbers separate into phases in solutions.

In this connection Slonimsky introduced the concepts *micro-* and *macroheterogeneity* of mixtures.

Mixtures formed from polymers which separate into phases in solution are always microheterogeneous, which is manifested in cloudiness of the films. Therefore, if an article has to be transparent, it cannot be prepared from polymers which are incompatible in solution. But if transparency is not necessary and the microheterogeneous mixtures have anomalous but fairly good mechanical properties, they are suitable for certain purposes.

It was assumed at first that the mechanical properties of polymer mixtures depend on their mutual compatibility. However,

it was later shown that they are considerably determined by the technological conditions for preparing a mixture; they depend on whether mixing occurs at a temperature which is higher or lower than the glass-transition temperature of polymers, and on the polymer which is a dispersion medium and which is a dispersed

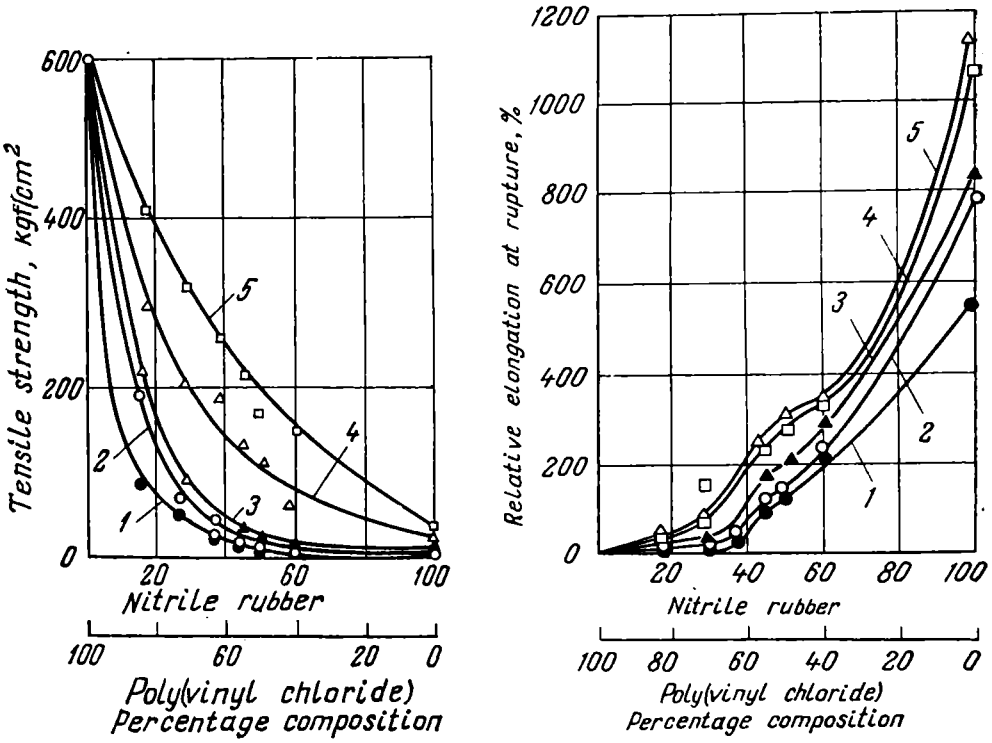

Fig. 19.3. Dependence of tensile strength (*a*) and relative elongation (*b*) on the composition of mixtures of PVC with nitrile rubbers:
1—11.7%; *2*—19.6%; *3*—28.8%; *4*—36.0%; *5*—49.9% of nitrile groups in rubber

phase. For example, when a mixture of PVC and CKH-26 is heated for seven minutes at 170 °C, its strength increases by 1.5-2 times. If the dispersion medium (matrix) is rubber, while the dispersed phase is rigid plastic, the mixture has elastic properties. Conversely, if the dispersion medium is rigid plastic, while the dispersed phase is rubber, the mixture is rigid. However, in both cases, two-phase mixtures can have higher strength in comparison with individual components. According to Kuleznev, this occurs because cracks either grow slower or stop growing in such systems. So, a crack which grows in the rigid matrix deforms a particle with a small modulus on meeting it; then, overstress diminishes and the crack stops growing. If a crack grows in a soft matrix, it rounds the dispersed rigid particles, its path increases and its growth is retarded.

Recently, it has been shown that the ability to form a continuous medium is determined by the difference in the rheological properties of individual components. It has been discovered that highly dispersed mixtures are formed if the viscosities of components are similar. In any incompatible mixture, a continuous dispersion medium is formed by a component which has the least viscosity of a melt. If the viscosity and elasticity of a component whose amount is the smallest are considerably greater than those of the main component, coarse-break-up systems are formed.

The most important property of polymer mixtures is their high resistance to multiple deformations in comparison with individual components.

To reinforce the rubbers, use is mainly made of resins based on phenol and amino aldehyde resins. They exhibit high reactivity and polyfunctionality, and are capable of changing properties in a wide range. Therefore, different results may be obtained when rubbers are reinforced by the same resins.

Among crystalline plastics, wide use is made of polyethylene (PE) and polypropylene, which have a highly ordered structure, high chemical stability and great mechanical strength. The greatest use is made of low-pressure PE. By the reinforcing action of PE, it competes with the best sorts of carbon black. In its presence, the strength of a mixture and relative elongation increase, and gas permeability (p. 629) decreases. On the other hand, in order to increase elasticity and impact strength, various rubber-like polymers are added to plastics (PVC, PMMA).

Hence, many works show that mixtures of two thermodynamically incompatible polymers can have very good mechanical properties, and some researchers are even inclined to believe that thermodynamic compatibilty is of no significance whatsoever. But this is not so, because good mixtures can be prepared not from all polymers by far, and therefore polymer compatibility remains a problem. On the contrary, many attempts are being made to estimate compatibility by various methods, which make it possible to determine the glass temperature of a system.

19.6. DETERMINATION OF GLASS-TRANSITION TEMPERATURES OF POLYMER MIXTURES

It has been shown in many works that several polymer mixtures have two glass-transition temperatures characteristic for each polymer. This implies that both polymers in a mixture act independently of one another. The presence of two glass-transition temperatures T_g is considered to be an indication of polymer incompatibility. One glass-transition temperature is observed for mixtures of compatible polymers, and its position continuously chang-

es on the temperature axis with polymer composition. To determine T_g of polymer mixtures, methods expounded in Chap. 8 are used.

The **method of mechanical losses.** Figure 19.4 gives a typical dependence of the mechanical loss tangent on temperature for incompatible polymers.

The **dielectric loss method** was first used for polymer mixtures by Mikhailov, who showed the presence of two maxima on the dielectric loss tangent versus temperature curves for a mixture of polystyrene and methyl methacrylate, whose position corresponded exactly to T_g of the components and did not change with composition. It was concluded that the components are incompatible.

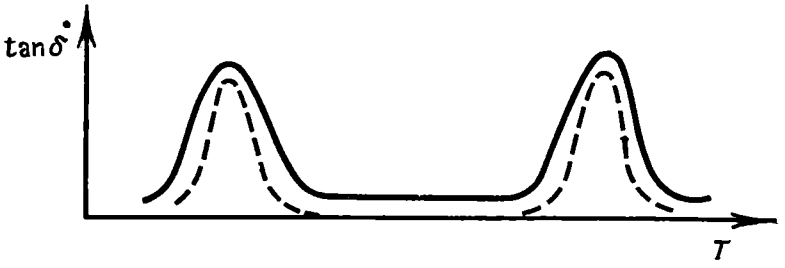

Fig. 19.4. Dependence of mechanical losses on polymer mixture composition

This method was used to show the presence of two maxima on tan δ versus temperature curves for several other polymer mixtures. It should be noted, however, that the method has several shortcomings owing to the difficulty in detecting the orientational component of dielectric polarization for nonpolar and highly polar polymers. When one of the components is such a polymer, it is expedient to control the position of the maximum of losses of another polymer and its change caused by the composition of a mixture. Two dependencies can be observed, as represented in Fig. 19.4. If the components are compatible, the maximum moves along the temperature axis continuously in conformity with the quantity of the second polymer added. If the components are incompatible, the maximum does not change its position with the composition.

The scanning calorimetry method for determining the heat capacity of a polymer mixture was recently used by Thies and coworkers. They detected two clear peaks, which exactly corresponded to the glass-transition temperatures of isolated components for mixtures of polystyrene and polyvinyl methyl ether.

The **method of determining refractive indices** was used by Jenckel for estimating T_g of the PVA-PMMA mixture. He discovered that the dependence n_D on temperature is expressed by a broken line with two inflections, which correspond to T_g of polymers.

Dilatometry for polymer mixtures was first used by Bartenev and coworkers. They studied the temperature dependence of the specific volume of the mixtures of НК-СКБ, НК-СКН-26 and СКН-18-СКН-40. For the first and third systems, they discovered a single T_g which depended on the ratio of the components, and they believe that this indicates the compatibility of these polymers. For the second system, two T_g were discovered, indicating the incompatibility of the components.

The **radiothermoluminescence (RTL) method** is based on the fact that polymers exposed at low temperatures begin to glow as temperature rises, the intensity of luminescence passing through the maximum in the temperature range where the mobility of segments becomes apparent, i.e., in the T_g range. The single T_g has been observed for the НК-СКБ and СКБ-СКН systems, i.e., for mixtures of rubbers which are of similar chemical nature. For the remaining seventeen systems studied, the authors found two T_g.

Hence, the study of transition temperatures gives certain information on polymer compatibility and shows that in many polymer compositions, the components act independently of one another and this indicates the absence of their mutual solubility.

19.7. POLYMER COMPATIBILITY DETERMINED BY VARIOUS METHODS

The compatibility of polymer pairs may be estimated by various methods. Estimations coincide for some systems. For example, the CN-PVA and CN-PMMA systems are compatible according to the results obtained by all the methods: they are mutually soluble polymers which form a one-phase system and have the single transition temperature. The PE-PI system is incompatible according to all the estimates, while for many other systems, umbiguous results have been obtained.

Proceeding from this, some researchers believe that it is most expedient to estimate the so-called exploitation compatibility of polymers, i.e., to determine within which limits and for which specific characteristics change in properties is allowed in the exploitation process. The term "technological" compatibility has also been coined; it implies satisfactory physicomechanical indices of polymer mixtures.

Undoubtedly, the physicomechanical properties of polymer mixtures should be studied at different temperatures and times, varying the regimes of technological preparation of mixtures. But such an abundance of terms does not clear up the problem. Many researchers have drawn attention to the fact that such terminology and the term "compatibility" in general cannot be successfully

used, and have indicated that the only correct approach is to estimate the thermodynamic stability of polymer-polymer systems. Moreover, all the aforementioned methods, including structural investigations, can only establish the presence or absence of compatibility, and they cannot give any information on its causes and on affinity between polymers. Only thermodynamics can give an answer to this question.

19.8. THERMODYNAMIC INVESTIGATION OF POLYMER-POLYMER SYSTEMS. THREE-COMPONENT SYSTEMS

Thermodynamic investigations of the polymer-polymer systems were begun by the work of Dobry, in which phase equilibrium was considered for some solvent 1-polymer 2-polymer 3 systems. For this purpose, moderately concentrated solutions, each of which

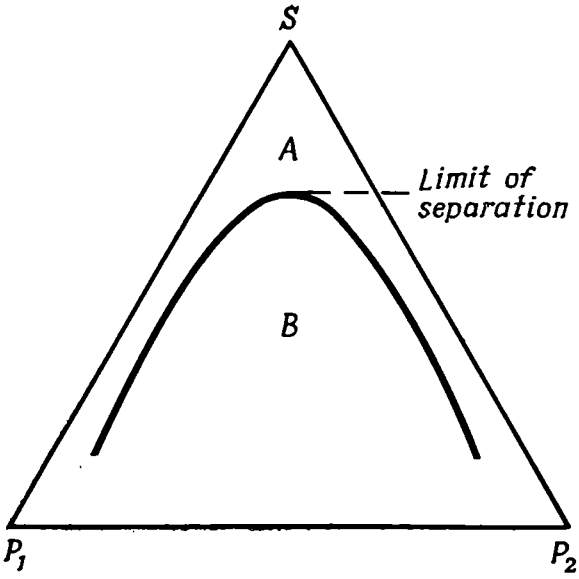

Fig. 19.5. State diagram of three-component system polymer I-polymer II-solvent

contained one of the polymers in a common solvent, were poured together. The cloudy solution was allowed to separate into phases, and the concentration of all the three components in each layer was analytically determined. Then, a triangular diagram was plotted by Rosebom's method, as shown on page 355. Binodals were obtained that separated the regions of stable and metastable systems, and that had the form of extremum curves (Fig. 19.5). The maximum concentration value of a solvent that causes phase separation (or the minimum concentration of polymers in a solution) is known as the *phase separation limit*, which the authors believe depends only on the nature of a polymer and

not on that of a solvent. They formulated the principle that polymers which separate into phases in one solvent do so in all the others.

This work gave an impetus to the theoretical works by Scott and Tompa.

Proceeding from the Flory-Huggins theory of solutions (Chap. 14), Scott derived the equation for critical parameters of interaction in systems containing two components 2 and 3:

$$\chi^s_{2,3} = \frac{1}{2}\left(\frac{1}{m_2^{1/2}} + \frac{1}{m_3^{1/2}}\right) \tag{19.1}$$

where m_2 and m_3 = degrees of polymerization of components.

It follows from the equation that:

(1) for two low-molecular liquids $m_2 = m_3 = 1$; $\chi^s_{2,3} = 2$;

(2) for polymer solutions in low-molecular analogues $m_2 = 1$, $m_3 = \infty$, $\chi^s_{2,3} = \frac{1}{2}$;

(3) for two polymers $m_2 = m_3 \to \infty$; $\chi^s_{2,3} = 0$.

Hence, according to the theory, polymers at $\chi_{2,3} > 0$, even if this quantity is very small, say 0.0025, are poor solvents in respect to one another, i.e., they are incompatible.

For three-component systems, three parameters of interaction are introduced:

between polymer 2 and solvent 1 . .	$\chi_{1,2}$
between polymer 3 and solvent 1 . .	$\chi_{1,3}$
between two polymers	$\chi_{2,3}$

Writing Eq. (14.32) for each of the three components, Scott solved the binodal equation for the simplest, so-called "symmetric" case, when $m_1 = m_2$ and $\chi_{1,2} = \chi_{1,3}$. The binodal obtained is represented in Fig. 19.6*a*. It is a symmetric curve with nodes parallel to the axis which corresponds to the binary polymer-polymer system. As $\chi_{2,3}$ increases, i.e., as polymer interaction worsens, the region of homogeneous solutions (outside the binodal) gradually diminishes. Consequently, Scott's theory confirmed the statement that the phase separation limit depends only on the nature of polymers and not on that of a solvent, and that polymers which separate into phases in one solvent do so in all the others.

Tompa has shown that the quality of a solvent should affect the phase separation limit, and that the region of homogeneous solutions diminishes (Fig. 19.6*b*) even for the symmetric case as χ increases, i.e., as the quality of a solvent worsens. At definite allowances, Tompa obtained an asymmetric binodal with unparallel nodes; the region of homogeneous mixing decreases with a growth of χ ($\chi = \chi_{1,2} = \chi_{2,3}$) in this case as well.

The unparallelism of nodes in a triangular diagram, as is well known, is always the outcome of different interaction between component 1 and two other components, i.e., its coefficient of distribution between them. For example, if component 1 has greater affinity for component 2 than for component 3, i.e., $\chi_{1,2} < \chi_{1,3}$, we obtain a diagram represented in Fig. 19.7*a*. Conversely, if $\chi_{1,2} > \chi_{1,3}$, the diagram has the form given in Fig. 19.7*b*. Consequently, the distribution of a solvent in two equilibrium conjugated

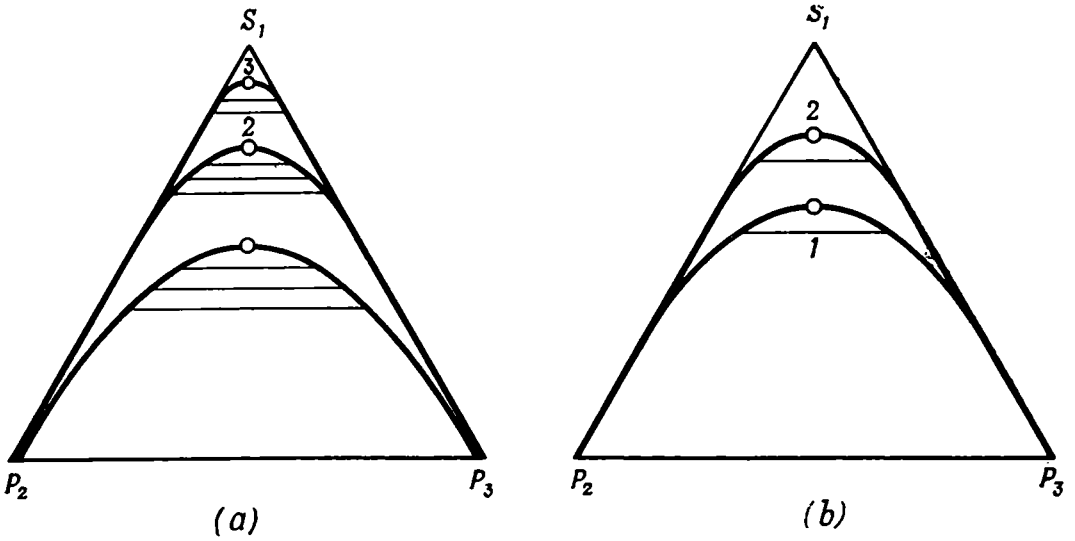

Fig. 19.6. Binodals of polymer-polymer-solvent systems. Symmetrical case: *a*—from 1 to 3 $\chi_{2,3}$ increases; *b*—from 1 to 2 χ increases

phases is more favourable for the one which is enriched with a polymer that has greater affinity for the solvent. Therefore, an increase in the difference of $\chi_{1,2}$ and $\chi_{1,3}$ should displace the binodal to the side that corresponds to a higher value of χ. As component 1 (solvent) is added, phase compositions become similar, the length of nodes diminishes and, when the compositions of the conjugated layers become identical, the node degenerates into a point. This is the critical point, which is not on the vertex of the curve, but on one of its branches.

Such binodals were obtained for three-component polymer systems by Kern and others. It is shown in these works that the phase separation limit depends on the difference $\chi_{1,2} - \chi_{1,3}$. This is seen especially clearly from the work by Hugelin and Dondos who showed the role of selectivity of a solvent, i.e., its preferential interaction with one of the polymers. This made it necessary to revise the Scott-Tompa theory, and this was done by Zeeman and Patterson and Hsy and Prausnitz. In these works, it is theoretically predicted that the region of homogeneous mixing should

sharply diminish as the difference $\chi_{1,2} - \chi_{1,3}$ increases. In this case, a very inconsiderable difference, e.g., $\chi_{1,2} = 0.40$ and $\chi_{1,3} = 0.45$ is significant. The authors indicate that the incompatibility of polymers in solution grows as the difference in the interaction of polymers with the solvent increases, and that this plays a considerably larger role than polymer-polymer interaction.

Hence, theory and experiments show that the separation of solutions of the same polymers should occur differently, depending on

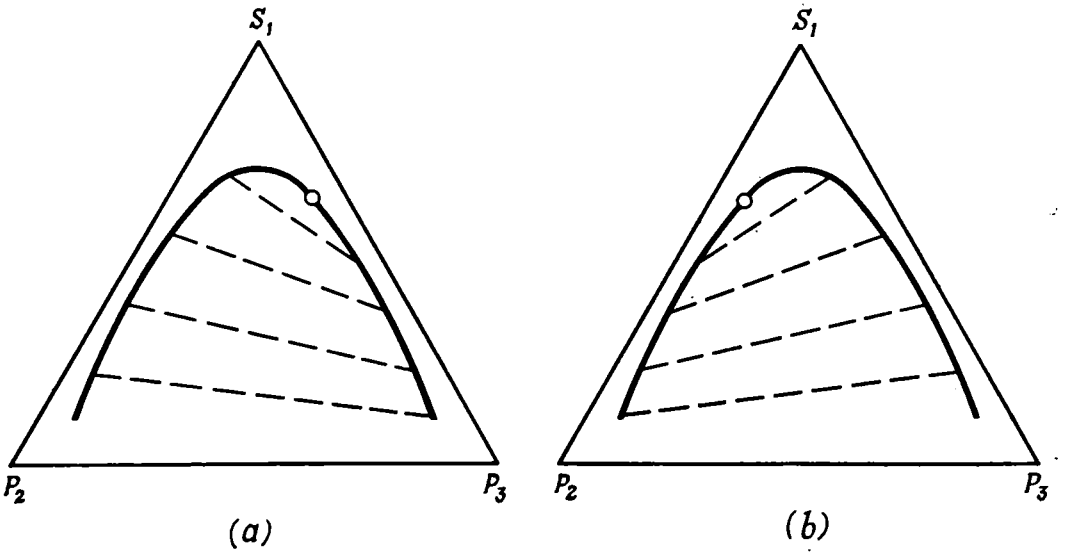

Fig. 19.7. Unsymmetrical binodals:
a—solvent mixes better with polymer P_2 ($\chi_{1,2} < \chi_{1,3}$); *b*—solvent mixes better with polymer P_3 ($\chi_{1,3} < \chi_{1,2}$)

the nature of a solvent. Moreover, there can be a case when two compatible polymers can separate in a solution at a definite value of the difference $\chi_{1,2} - \chi_{1,3}$. Hence, phase separation in solutions is not always the evidence of polymer incompatibility. For example, a diagram like the one given in Fig. 19.7 is observed for the acetic acid-water-chloroform system. But the phase separation of the three-component system does not mean at all that acetic acid and water are incompatible. Everything depends on the parameters of interaction between each component with the other two; in solution, they may differ from values characteristic of binary mixtures. For example, it was shown that the parameter $\chi_{2,3}$ depends on the difference $\chi_{1,2} - \chi_{1,3}$. It follows that the statement formulated by Dobry cannot be held as a true one, and cases are now known when two polymers separate in one solvent but do not in another. Therefore, the common solvent method does not make it possible to obtain reliable results concerning the state of a polymer mixture without a solvent.

The investigation of the properties of solutions of two polymers is very important when a polymer mixture is obtained from solutions. But it should be noted that a deviation of the values of viscosity or density of solutions from additivity should by no means be regarded as an indication of compatibility or incompatibility of polymers, as is done in some works. The viscosity of even ideal solutions is not formed additively from the viscosity of the components. The mixing of liquids and the dilution of polymers is, as a rule, accompanied with a decrease or increase in volume (p. 399), i.e., the volumes and densities of all the solutions are not additive quantities, but this does not mean that the components are incompatible.

Hence it follows that the most correct and necessary thing to do is to consider binary polymer-polymer systems thermodynamically.

19.9. THERMODYNAMICS OF BINARY POLYMER-POLYMER SYSTEMS

The only correct estimation of the thermodynamic compatibility and affinity of two components is the free energy of their mixing, which is determined quite simply for solutions of polymers in low-molecular liquids (Chap. 13). However, the experimental methods expounded above are unsuitable for the polymer-polymer system, because the vapour pressure of a polymer cannot be measured or the osmotic pressure cannot be determined for such a system. Therefore, until recently, no one determined the free energies of polymer mixing. Moreover, back in 1947, Gee calculated the entropy of mixing for two polymers and showed that it is negligibly small. For example, when two components, each being a cubic centimetre, are mixed, the entropy of mixing is

for two liquids	8.3 cal
liquid + polymer	4.15 cal
two polymers	0.0083 cal

Hence the conclusion that when polymers are mixed together, changes in entropy are practically equal to zero and the free energy of mixing is exactly equal to the enthalpy of mixing. This principle prevailed for 30 years, and researchers concentrated their attention on the determination of the enthalpy or heat of polymer mixing. It is now shown that this is not so, and we will consider this in detail.

19.9.1. Enthalpy of Mixing of Two Polymers

It is impossible to determine the enthalpy of mixing of two polymers directly in a calorimeter. It can be calculated only by using

Hess' law and several thermochemical equations, e.g.,

$$1\text{ g of polymer I} + \text{solvent} = \text{solution I} + Q_{\text{I}}$$

$$1\text{ g of polymer II} + \text{solvent} = \text{solution II} + Q_{\text{II}}$$

$$\text{solution I} + \text{solution II} = \text{solution III} + Q_{\text{IV}}$$

Evidently, solution III can be obtained also in another way by mixing two polymers and dissolving this mixture. Then,

$$1\text{ g of polymer I} + 1\text{ g of polymer II} = \text{mixture} + Q_X$$

$$\text{mixture} + \text{solvent} = \text{solution III} + Q_{\text{III}}$$

Since enthalpy is a function of state, it does not depend on the path of a process, and therefore

$$Q_{\text{I}} + Q_{\text{II}} + Q_{\text{IV}} = Q_X + Q_{\text{II}} \tag{19.2}$$

Hence, the heat of mixing of two polymers

$$Q_X = Q_{\text{I}} + Q_{\text{II}} + Q_{\text{IV}} - Q_{\text{III}} \tag{19.3}$$

Hess' law can be used only if the amount of a solvent in every experiment is so great that the heat effect would be null when it is added further. Then, the heat of mixing of two dilute solutions (I + II) $Q_{\text{IV}}=0$, which is confirmed experimentally, and Eq. (19.3) assumes the form

$$Q_X = Q_{\text{I}} + Q_{\text{II}} - Q_{\text{III}} \tag{19.4}$$

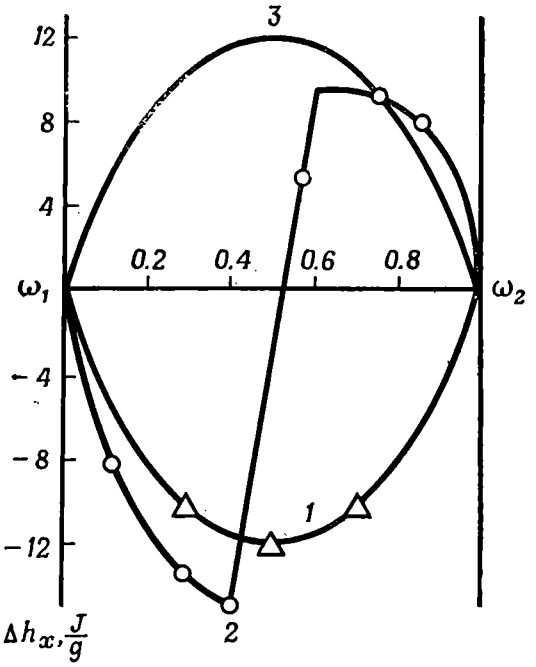

Fig. 19.8. Dependence of enthalpy of mixing of polymers on polymer mixture composition:

1—exothermal mixing in the entire composition range; *2*—enthalpy of mixing changes sign; *3*—endothermal mixing in the entire composition range

Hence, the task is to measure the heat of dilution of each polymer and their mixture, say a film obtained from a solution of two polymers, in a common solvent.

This task can be simplified by measuring the heat of solution of such a film and the mechanical mixture (m.m.) of two components taken in the same ratio:

$$1\text{ g of m. m.} + \text{solvent} = \text{solution I} + Q_{\text{I}}$$

$$1\text{ g of film} + \text{solvent} = \text{solution II} + Q_{\text{II}}$$

whence

$$Q_X = Q_I - Q_{II} \tag{19.5}$$

Slonimsky and Struminsky used this method to determine the heat of mixing of many polymer pairs with the same ratio of the components. The authors drew the conclusion that, in most cases, systems which do not separate into phases in solutions are characterized by negative values of heats of mixing ($\Delta H < 0$), while systems which separate into phases, by positive values ($\Delta H > 0$). There were some exceptions to this rule ($\Delta H = Q$).

Later, such investigations were carried out by Mikhailov and Fainberg and Tager and Bessonov. In the latter work, the enthalpies of mixing of polymers at different ratios of the components were determined. Figure 19.8 shows that there is exothermal mixing in the system of mutually soluble components (CN-PVA) in the entire polymer composition range; the curve is convex down and the maximum value of $\Delta h_X \cong -10$ cal. For the remaining systems which were investigated, the concentration dependence of the heats of mixing is represented by a curve that consists of three regions. Such curves are observed for some binary liquid-liquid systems that separate into phases.

19.9.2. Free Energy of Mixing of Polymers

Recently, A. A. Tager proposed the method of calculating the free energy of mixing of two polymers based on the fundamental principle of thermodynamics that Gibbs' free energy is a function of state of a system and, consequently, it does not depend on the path of a process, but is determined only by the difference in the final and initial states. Therefore, the same cycle of equations can be written for the free energy of mixing as for the enthalpy of mixing.

If the initial state is one gram of polymer I, one gram of polymer II and a sufficiently large amount of a solvent, the final state will be a solution of both components in this solvent. This solution can be obtained in two ways:

(1) by preparing solutions of each of the two polymers and pouring them together;

(2) by preparing a mixture of these polymers and dissolving them in a large amount of a solvent.

All that can be written in an equation system.

First way:

$$1 \text{ g of polymer I} + \text{solvent} = \text{solution I} - \Delta G_I$$

$$1 \text{ g of polymer II} + \text{solvent} = \text{solution II} - \Delta G_{II}$$

$$\text{solution I} + \text{solution II} = \text{solution III} - \Delta G_{IV}$$

Second way:

$$1 \text{ g of polymer I} + 1 \text{ g of polymer II} = \text{system } X^* - \Delta G_X$$

$$\text{system } X + \text{solvent} = \text{solution III} - \Delta G_{III}$$

Evidently, the sums of the free energies of the processes which are occurring in two ways should be equal. Consequently,

$$-\Delta G_X - \Delta G_{III} = -\Delta G_I - \Delta G_{II} - \Delta G_{IV} \qquad (19.6)$$

The sited thermodynamic cycle is valid, like Hess' law, if the solvent is taken in a large amount. In this case, it can be allowed that when two very dilute solutions I and II are poured together, $\Delta G_{IV} = 0$.

Then,

$$-\Delta G_X = \Delta G_{III} - (\Delta G_I + \Delta G_{II}) \qquad (19.7)$$

where ΔG_I, ΔG_{II} and ΔG_{III} = free energies of mixing of the first and second polymers and their mixture, respectively, with a common solvent per gram of the polymer or per gram of their mixture.

If we mix m_1 grams of polymer I and m_2 grams of polymer II, Eq. (19.7) will assume the form

$$-\Delta G_X = (m_1 + m_2)\Delta G_{III} - (m_1 \Delta G_I + m_2 \Delta G_{II}) \qquad (19.8)$$

Dividing both parts of (19.8) by $(m_1 + m_2)$, we obtain the average free energy of mixing Δg_X for the formation of one gram of a polymer mixture:

$$\Delta G_X = \Delta G_{III} - (w_1 \Delta G_I + w_2 \Delta G_{II}) \qquad (19.9)$$

where w_1 and w_2 = weight fractions of polymers in a "dry" polymer composition.

The values of ΔG_I, ΔG_{II} and ΔG_{III} can be determined experimentally by methods expounded in Chap. 13. To this end, for example, the vapour pressure of a common solvent over the solutions of both polymers and their mixture can be measured at constant temperature, and the values of $\Delta\mu_1$, $\Delta\mu_2$ and Δg^m can be calculated. The dependence of Δg^m on the composition of solutions, expressed in weight fractions, has the ordinary form of smooth curves, which lie in the negative region and are convex down (Fig. 19.9). If tangents are drawn to these curves at the point $w_2 = 0$, they will cut off segments on the ordinate axis that are equal to the free energies of mixing of one gram of a polymer component with a common solvent. Substituting these quantities in Eq. (19.9), we obtain Δg_X.

* System X can be either a one-phase solution or a two-phase system.

Such a method was used to calculate the free energies of mixing for several polymer mixtures. It was found that the dependence of the average free energy of their formation Δg_X on polymer composition is expressed by three types of curves characteristic of stable and unstable systems, and systems which separate into phases in a definite composition region (Fig. 19.10).

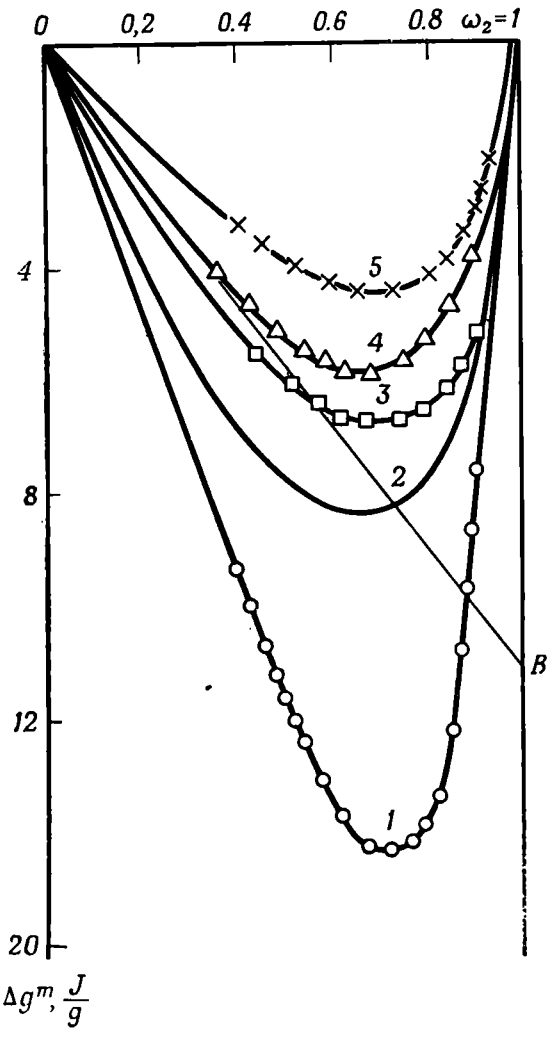

Fig. 19.9. Typical concentration dependence of free energy of mixing of individual polymers (*1* and *5*) and their mixtures of different composition (*2-4*) with a common solvent

For example, the CN-PVA system is formed spontaneously with diminution of free energy. The curve $\Delta g_X = f(\omega_2)$ is in the negative region and is concave down, i.e., the main condition of the thermodynamic stability of binary systems $\frac{\partial^2 g}{\partial x^2} > 0$ is accomplished (p. 391).

For the PVC-PMMA and CA-PVA systems, this dependence is expressed by curve *2*. It should be borne in mind that points *A* and *B* of such curves correspond to the points of binodal (p. 392), i.e., the line that separates the stable region from the metastable one, which is apparently very great for polymer-polymer systems. For the metastable region, stability conditions are maintained $\left(\frac{\partial \mu_1}{\partial x_2} < 0, \frac{\partial \mu_2}{\partial x_1} < 0 \text{ and } \frac{\partial^2 g}{\partial x^2} > 0\right)$, i.e., this state is very close to equilibrium states. The region of absolute instability of such polymer compositions is apparently not attained practically owing to their high macroviscosity. The negative value of Δg_X and the positive value of its second derivative are a guarantee of the practically stable state of such systems.

But there are polymer compositions for which $\Delta g_X > 0$ and $\frac{\partial^2 g}{\partial x_2^2} < 0$ (curve *3*) in the entire composition range. They are ther-

modynamically unstable systems. The PMMA-PBMA, PVC-СКБ and PVC-СКН-18 systems are among them.

Thermodynamically stable systems are formed from mutually soluble components, and they are one-phase ones. Metastable two-phase systems are formed from components which are mutually

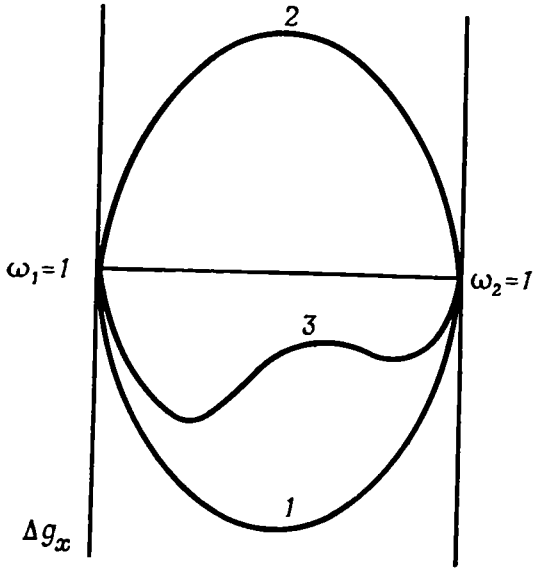

Fig. 19.10. Dependence of free energy of mixing of polymers with one another on the mixture composition:

1—thermodynamically stable systems; *2*—metastable two-phase systems; *3*—thermodynamically unstable systems

insoluble but which dissolve well on the segment level. This ensures the presence of thick transition layers when they are appropriately dispersed, and their practical stability and good properties.

Thermodynamically unstable systems apparently cannot possess good properties and their exploitation properties cannot be guaranteed.

19.9.3. Entropy of Mixing of Two Polymers

The determination of the free energy of mixing of two polymers has allowed A. A. Tager and coworkers to calculate, for the first time, the entropy of their mixing by using experimental data. The calculation was made according to the equation $\Delta g_X = \Delta h_X - T\Delta s_X$. These data are given in Figs. 19.11, 19.12, which show that, contrary to the existing concepts, the entropy of mixing of polymers is not equal to zero, and that it does not play a smaller role than the enthalpy of mixing. For various systems, it has a different value and diverse signs.

For example, for the thermodynamically stable CN-PVA system, $\Delta s_X < 0$, like Δh_X in the entire composition region. For the PMMA-PBMA system, $\Delta s_X > > 0$, like Δh_X in the entire composition region, while for many other systems, Δs_X changes the sign when the composition changes.

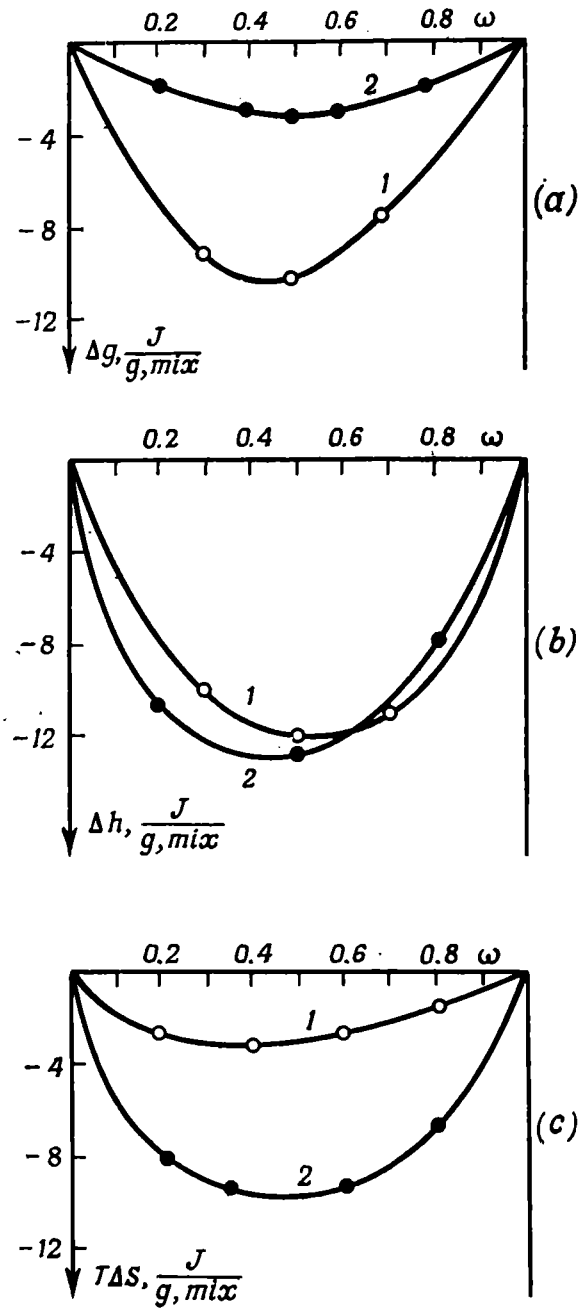

Fig. 19.11. Free energy (*a*), enthalpy (*b*) and entropy (*c*) of mixing for a system: *1*—CN-PVA; *2*—CN-PMMA

Why did an incorrect concept of the allegedly zero entropy of mixing of polymers exist for a long time? This is connected with the fact that equation according to which Gee made his calculation, is derived only for the combinatorial entropy of mixing that is determined by rearrangements of molecules of two different kinds. It is quite clear that large macromolecules of low mobility cannot change places with one another. Therefore, ΔS_{comb} for polymer mixtures should have a low value. But there is a noncombinatorial contribution to the entropy of mixing that is due to macromolecular interaction and is exhibited in greater or smaller degree of ordering of a system. This contribution should be considerable also for polymer mixtures. This follows from simple considerations which are connected, for example, with the impossibility for polymers of different kind to form common structures.

If the structure of a mixture is more or less ordered than the structure of individual components, the entropy of mixing can be either negative or positive.

Negative entropy of mixing indicates that the CN and PVA macromolecules in a mixture are packed more orderly than in individual components. The positive value of ΔS_x implies that macromolecules in a mixture are in a more disordered state than in pure substance. Thus, the PMMA and PBMA macromolecules cannot be packed together.

These data show that the true cause of the mutual solubility of two polymers is the possibility or impossibility for them to form

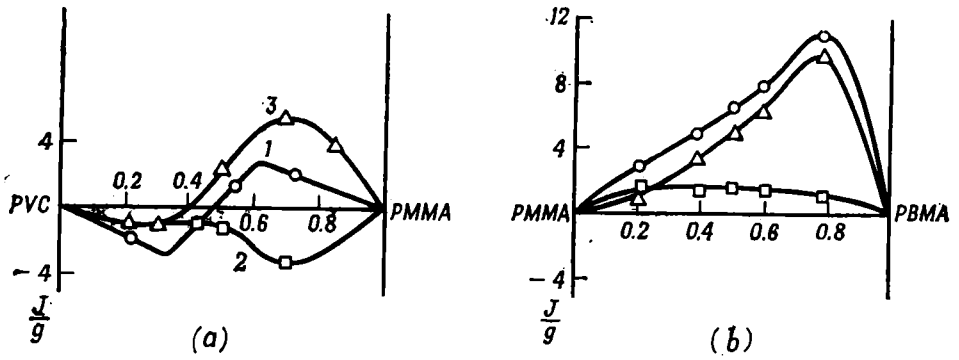

Fig. 19.12. Free energy (*1*), enthalpy (*2*) and entropy (*3*) of mixing for a system: *a*—PVC-PMMA; *b*—PMMA-PBMA

dense compatible structures. If this is possible, they mix together, and if not, they do not mix. This applies not only to crystalline, but also to amorphous polymers.

The given data confirm the theoretical calculations made by Flory and coworkers, who used the new theory of solutions (p. 449). The calculations were made for the polyethylene-polyisobutylene system, which is considered to be incompatible according to all the data. The authors have shown that these polymers mix together with increasing free energy and with negative entropy. In their work, they especially emphasize that the entropy term, whose role is not smaller than that of the enthalpy of mixing, must not be neglected when polymers mixed.

19.9.4. Phase Diagrams of Polymer-Polymer Systems

The temperature dependence of the solubility of components is very important. It is significant also for polymer mixing. Do polymers mix better or worse on heating? To answer this question, it is necessary to study phase diagrams, which practically cannot be obtained for two high-molecular polymers.

In literature, there are some phase diagrams for oligomers. Figure 19.13 gives a diagram obtained by Allen and coworkers. When the molecular masses of both components are sufficiently

low, we can observe the curve of mixing with UCST, which is in the 120-200 °C region and grows as molecular mass increases. Mac Intyre and others have shown that the UCST of solutions of polyisoprene (PIP) and polystyrene (PS) with a molecular mass of 1000 is —30 °C; for solutions of these components with $M =$ $= 2000\text{-}3000$, UCST = +56 °C. For samples of these polymers with a molecular mass of 20 000, the mixture is heterogeneous in the entire composition region and temperature range.

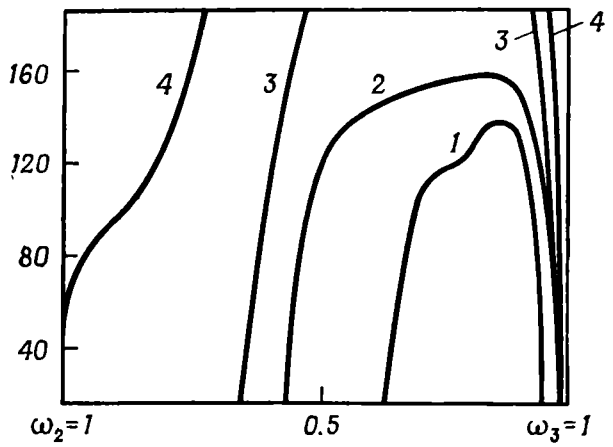

Fig. 19.13. Phase diagram of a system polyisobutylene-polydimethylsiloxane for different ratios of molecular masses of components:
1—250 : 850; *2*—250 : 1350; *3*—440 : 1350; *4*—250 : 170 000

Proceeding from these data, it may be assumed that for polymers of a high molecular mass, UCST should be in an unattainably high temperature range. After analysing the data on the heats of dilution of polymers and signs of temperature coefficients of solubility, connected with them, Tager and Bessonov concluded that it was impossible for UCST to exist for polymer mixtures.

Conversely, according to the data given by several researchers, polymer intermiscibility worsens with an elevation of temperature. This was noticed for mixtures of polyethylene and polyisobutylene, polystyrene and polyvinyl methyl ether and other mixtures. The opinion is expressed that polymer-polymer systems are characterized by low critical solution temperatures (LCST).

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CHAPTER 20

Polymer Sorbents and Porous Structure of Polymers

Polymers are increasingly used as sorbents, i.e., as materials which absorb, or sorb, ions and molecules of various substances from different media. They are diverse ion-exchange resins, and also polymer sorbents which do not contain ionogenic groups and are used in gel chromatography (p. 367). Sorption processes play a considerable part in the interaction between polymer fibres and various reagents and dyes, in gas and vapour permeability of polymeric materials (Chap. 21), and so forth. Therefore, it is expedient to consider the specific features of polymer sorbents, the regularities of the formation of a porous structure of polymers and the methods of its estimation, the mechanism of sorption of low-molecular liquids and vapours on polymers, and ion-exchange resins.

20.1. SORPTION AND ADSORPTION

Sorption is absorption of one substance by another, such as absorption of one liquid by another or of gases by liquids. But in most cases the term applies to absorption of molecules of gases, vapours, liquids, or ions, by solids; this process may occur according to two mechanisms:

(1) A body may absorb a substance only by its surface, either external or internal (the latter surface is very large for the so-called *porous* solids). Such a process is known as *adsorption.* The adsorbing body is known as the *adsorbent*, while the substance being absorbed, as the *adsorbate* or the *adsorptive.* This process is divided into *physical adsorption*, when the adsorbate interacts with the adsorbent by the van der Waals forces, and *chemisorption*, when chemical reactions occur between them.

(2) The molecules of the substance being sorbed penetrate into a solid, into the force field, which exists between its atoms, ions or molecules in the entire volume. There may be two processes in this case as well: gas or vapour may either *dissolve* in a solid or *form a chemical compound* with it.

In most cases, the processes of adsorption and dissolution occur simultaneously, and they are both termed *sorption.* The sorbing body is known as the *sorbent*, while the substance being absorbed or dissolved, as the *sorbate.*

Sorption or adsorption occur because the sorbent creates a force field. It was believed in the classical theory of physical adsorption worked up for mineral sorbents (activated charcoal, metal oxides, and so forth), that the sorbate molecules undergo changes as they get into the force field of a sorbent, while the sorbent remains "unperturbed". This gave rise to the concept of an "inert" sorbent. However, as early as the 1940's, Hill indicated that the existence of an inert sorbent should be regarded as a hypothetical case, and that the absorbent undergoes changes under the action of the sorbate in any adsorption process. The matter was only the degree of its perturbation.

Recently, it has been experimentally shown that, in adsorption, the electron shells of atoms of mineral sorbents are deformed and, in some cases, their structure is rearranged, which is expressed in slight swelling, i.e., in a change in volume. But mineral sorbents undergo inconsiderable changes in volume. For example, when activated charcoal is saturated to the maximum with vapours of organic liquids, the change in volume constitutes 1×10^{-3} cm^3/g, and it is neglected. Such sorbents are considered to be practically rigid, and it is believed that the adsorbate occupies the pores available without changing the pores.

20.2. POROSITY AND THE METHODS OF ITS ESTIMATION

The concepts of "porosity" and "pores" originated when solid mineral sorbents and catalysts were being considered. According to Dubinin's definition, pores are "voids or spaces in solids". *Porosity is a property of solids that is due to their structure and is expressed in the presence of voids (pores) between separate grains, layers, crystals and other elements of a coarse structure of a solid.* This definition emphasizes the fact that the concept of porosity can be applied to solids, and that pores are space not between molecules, but between supermolecular structures.

The porosity of a sorbent is estimated quantitatively by several parameters: specific surface S_{sp}, total pore volume W_0, pore radius r and the differential curve of radial distribution of pore volumes.

There are several methods of estimating these parameters that have been worked out for mineral sorbents and are used also for polymers. Each of them covers a definite range of pore dimensions.

Method	Pore size, cm
Sorption	10^{-7}-10^{-5}
Mercury porosimetry . .	10^{-7}-10^{-3}
Electron microscopy . .	10^{-6}-10^{-4}
Optical microscopy . .	10^{-4}
X-raying	10^{-8}-10^{-5}

The most direct method is electron microscopy, which makes it possible to determine not only the dimensions, but also the shape of pores. It is used for studying mineral sorbents and polymers.

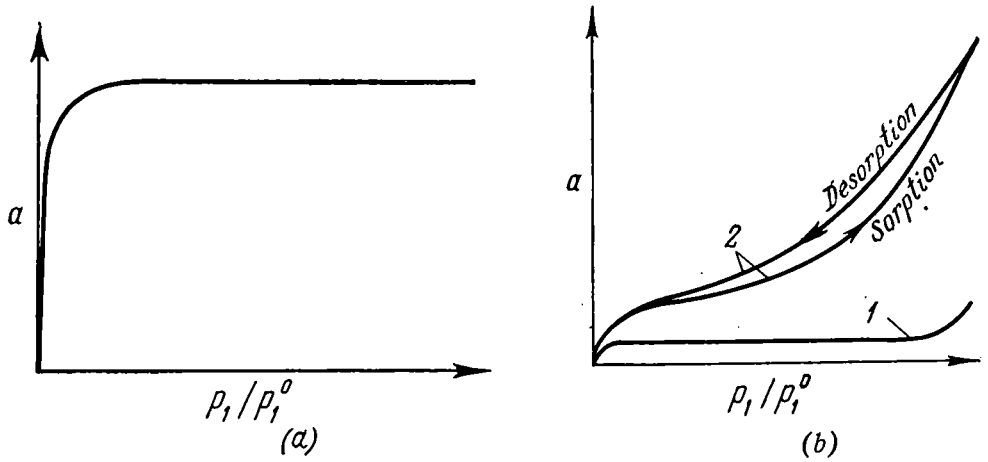


Fig. 20.1. Typical sorption isotherms of vapours on sorbents:
a—uniformly fine-porous; *b*—nonporous (*1*) and sorbents with transitional pores (*2*)

However, methods of preparing objects have still not been worked out sufficiently well for polymer sorbents. Use is also made of the X-raying which makes it possible to determine the radii of fine pores. But the most common are the classical sorption method and mercury porosimetry.

The sorption method consists in the determination of the amount of vapours of a low-molecular liquid that are sorbed by a body at different vapour pressures and in the plotting of the isotherms of sorption and desorption with the subsequent calculation, on their basis, of S_{sp}, W_0 and $\bar{r}_{av}$ and the differential distribution curves (DDC).

The amount of sorbed vapour is measured either by an increase in the mass of a sorbent with the aid of a very sensitive spiral balance (McBain's gravimetric method) or by the loss of vapour in a definite volume calibrated beforehand (volumetric method).

Sorption isotherms may be S- or Γ-shaped, depending on porosity (Fig. 20.1). The curves of sorption and desorption may not coincide, i.e., there may be so-called sorption hysteresis.

20.2.1. Calculation of Specific Surface Area of Sorbent

The following equation was suggested for calculating the specific surface area of a sorbent with S-shaped sorption isotherms by Brunauer, Emmet, and Teller (BET method).

$$\frac{P/P_0}{a(1-P/P_0)} = \frac{1}{Ca_m} + \frac{C-1}{Ca_m} \cdot \frac{P}{P_0} \qquad (20.1)$$

where P = equilibrium vapour pressure of sorbate per sorbent
P_0 = saturated vapour pressure of sorbate at the same temperature
a = amount of substance sorbed, mmole/g
a_m = amount of substance in continuous monomolecular layer, mmole/g
C = constant.

According to Eq. (20.1), the $\frac{P/P_0}{a(1-P/P_0)}$ vs. P/P_0 plot is a straight line, from the slope k and ordinate intercept b of which the values of a_m and C can be calculated:

$$a_m = \frac{1}{k+b} \quad C = \frac{k+b}{b} \qquad (20.2)$$

Knowing the area ω occupied by one molecule of a sorbate in a monomolecular layer and the number of molecules $a_m N_A \times 10^{-3}$ (N_A being Avogadro's number), we can calculate the specific surface area of the sorbent:

$$S_{sp} = a_m \omega N_A \times 10^{-7} \text{ m}^2/\text{g}$$

The area occupied by one molecule is calculated from the equation

$$\omega = 4 \times 0.866 \left(\frac{M}{4\sqrt{2}\, dN_A}\right)^{2/3} \qquad (20.3)$$

where M = molecular mass of sorbate
d = its density.

20.2.2. Calculation of Total Pore Volume of Sorbent

The total pore volume of uniformly fine-pore sorbents is calculated by means of the equation of Dubinin and Radushkevich:

$$\log a = \log \frac{W_0}{V} - 0.43B \left(\log \frac{P_0}{P}\right)^2 \qquad (20.4)$$

where V = volume of 1 mole of sorbate
W_0 = volume of liquefied vapour in a state of saturation, equal to the total pore volume
P = equilibrium vapour pressure of sorbate over sorbent
P_0 = saturated vapour pressure of sorbate
B = constant
a = amount of sorbate.

In $\log a$ versus $(\log P_0/P)^2$ coordinates Eq. (20.4) is represented by a straight line, the ordinate intercept of which b is equal to $\log W_0/V$. The total pore volume of sorbent W_0 is calculated from the size of this intercept.

Equation (20.4) holds for fine-pore sorbents. The total pore volume of large-pore sorbents is calculated from the equation

$$W_0 = aV \tag{20.5}$$

where a = amount (moles) of sorbate maximally taken up by 1 g of sorbent (determined from the sorption isotherm at $P/P_0 = 1$)
V = volume of 1 mole of sorbate.

The vapours of various inert organic substances can be used as sorbates for estimating the porosity of mineral and polymeric sorbents. It should be noted, however, that the size of sorbate molecules may affect the values of S_{sp} and W_0. For this reason, depending on the organic substance used, one measures the "benzene porosity", "*n*-hexane porosity", etc. The highest S_{sp} and W_0 values, other conditions being equal, are usually observed when the sorbate molecules are of the smallest size, enabling them to penetrate into the finest pores. From this point of view it is very convenient to use low-temperature nitrogen or krypton vapours, since the molecules of these gases are much smaller than those of organic substances. Nitrogen porosity is greater, as a rule, than benzene or methanol porosity.

20.2.3. Pore Radius and DDC

Knowing S_{sp} and W_0, one may calculate the average pore radius by the equation

$$\bar{r}_{av} = \frac{2W_0}{S_{sp}} \times 10^4 \text{ Å} \tag{20.6}$$

Kelvin's equation is used for a more precise determination of the pore radius:

$$r_K = \frac{2\sigma V}{RT \ln P_1/P_1^0} \tag{20.7}$$

where σ = surface tension of a sorbate
V = volume of one mole of a sorbate
R = gas constant (8.37×10^7 erg/deg. mole)
T = temperature, K.

The differential curves of radial distribution of a pore volume are calculated on the basis of desorption isotherms, which are divided, for this purpose, into several intervals that correspond to different stages of desorption. For every interval, a calculation is made of the number of millimoles of a desorbed substance Δa, the quantity Δr, i.e., the difference in radii $r_1 - r_2$, which correspond to the two extreme values of P_1/P_1^0 of this interval, and the average radius of pores $\bar{r}$, which are emptied at a given stage:

$$\bar{r} = \frac{r_1 + r_2}{2} \tag{20.8}$$

The value of desorption expressed in the volume of liquefied vapour ΔV is then calculated,

$$\Delta V = \Delta a V \tag{20.9}$$

where V is the volume of one mole of a sorbate, and a graph is then plotted in the coordinates $\Delta V/\Delta r = f(\bar{r})$.

When the sorption method is used, account should be taken of the fact that it has some limitations:

1. It cannot be used to calculate voids with $r < 6$-7 Å, because the amount of a substance sorbed by them is beyond the sensitivity limit of the method.

2. The quantities of W_0 calculated by Eqs. (20.4) and (20.5) do not reflect the true value of the total pore volume, but are essentially the maximum volume of adsorption space, which depends on the dimensions of the molecules being sorbed. The larger these dimensions, the less accessible are the fine pores of a sorbent for them and the smaller is the value of W_0. Therefore, to estimate the dimensions of fine pores, use is made of the sorption of small molecules, whether of nitrogen or argon, and it is effected at temperatures of their vapour condensation (low-temperature sorption). In this case, "nitrogen porosity" is greater than "benzene porosity" for mineral sorbents.

3. The parameters of a porous structure depend on the chemical composition of the sorbent surface that affects both the area occupied by a sorbate molecule in the adsorption layer, entering the BET equation, and the degree of wetting of a surface by a liquid, i.e., the process of capillary condensation. The poor wetting of a surface with the same pore size hinders capillary condensation and reduces the values of the parameters of a porous structure.

4. Pore radii calculated by Eq. (20.7) are not true values of pore radii. They are in essence radii of concave menisci of a liquid which has condensed between the adsorption layers on the pore walls. Therefore, to calculate the true value of pore radii, a correction for the thickness of the adsorption layer must be introduced.

5. The sorption method cannot be used to estimate the size of very large pores, since their walls are considerably away, it is difficult for polymolecular layers to merge in them, and therefore the process of capillary condensation is absent. The porous structure of solids in a wider range of pore dimensions can be studied by means of mercury porosimetry.

20.2.4. Mercury Porosimetry

The method of mercury porosimetry consists both in the measurement of the volume of mercury which penetrates into the pores of a material at given pressures and in the determination of the radii of pores filled up by mercury. This method makes it possible to cover a very wide range of pore radii, i.e., from thirty to hundreds of thousands of angstroms. Larger pores with r ranging from 50 000 Å to 100 000 Å are filled up at lower pressures of the order of one atmosphere. To fill up fine pores, use is made of higher pressures, which may attain 2500-4000 atm as the pore dimensions decrease. Therefore, two devices are usually used: porosimeters of low and of high pressures.

The pore radius is calculated by the equation

$$r = \frac{2\sigma \cos \theta}{P} \tag{20.10}$$

where σ = surface tensions of mercury at experiment temperature
θ = contact angle
P = given pressure, kg/cm².

Knowing V and r, we can plot the integral curves of radial distribution of the pore volume, which are differentiated in order to obtain the differential distribution curves in the coordinates $\Delta V/\Delta \log r = f(\log r)$.

When use is made of the method of mercury porosimetry, one comes across difficulties connected with the choice of the numerical values of surface tension of mercury and the contact angle θ which depend on the nature and smoothness of the surface and can change with pressure. Owing to the wrong estimation of the values of σ and θ, and to their possible change in the course of an experiment, the error in the determination of pore sizes may reach 30-40 per cent. In addition, the high pressures may cause the dis-

integration of the sorbent structure. Therefore, this method cannot be regarded as an absolute method of determining pore dimensions.

20.3. SPECIFIC FEATURES OF POLYMER SORBENTS

Polymer sorbents have several specific features which are connected with the entire set of their properties and polymer structure. Account should be taken of these specific features when their porous structure is being determined and when they are being used.

1. Polymers exist not only in a solid state, but also in a rubber-like state, and therefore the question of the competence of using the concepts of "pore" and "porosity" naturally arises. It is quite evident that these concepts are fully applicable to solid polymers (glassy and crystalline), whose voids practically do not change in time. From the standpoint of the definition given on page 594, voids or "holes" which exist in liquids and elastic polymers, i.e., voids of a fluctuational nature that continuously change their shape and dimensions, cannot be identified with pores. However, permanent voids which are created under definite conditions, such as in spongy rubbers or plastic foams, can apparently be called pores.

2. Unlike classical mineral sorbents, polymers, as a rule, swell in the course of sorption, i.e., they undergo considerable perturbations which are expressed in the change of their volume and structure. These perturbations depend on the thermodynamic affinity of a sorbate for a polymer (p. 381). The greater the affinity, the more does the structure of a polymer change.

The free volume which exists in a swollen polymer or in a gel, like in any liquid, has a fluctuational nature, and therefore it cannot be identified with porosity. It should be indicated in this respect that the concepts of the "porosity of polymers in a hydrated state", "pseudoporosity" and "latent porosity", found in literature, have no physical meaning.

To correctly determine the parameters of a porous structure of polymers, it is necessary to select, for every polymer, sorbates in which it practically does not swell and this should be ascertained by experiments carried out beforehand. We shall conditionally call such sorbates "inert" in contrast with "noninert" sorbates in which a polymer swells. This is a conditional name, because there are no absolutely inert sorbates and sorbents (p. 610). From this viewpoint, it is best to use the vapours of nitrogen or argon, especially since their molecules are not very large. But this is accompanied with sorption at low temperature, and therefore we do not always obtain correct results, which are determined also by the specific features of polymeric sorbents.

3. Low-temperature sorption of nitrogen vapours can be employed only for polymers whose coefficient of volume thermal expansion α is of the order of 10^{-6} deg^{-1}, i.e., when it is approximately the same as that of activated charcoal. In this case, when temperature drops by 200° (from 25 °C to —195 °C), the specific volume of a sorbent may change only by 0.002-0.003 cm^3/g, i.e., the porosity of a sample practically does not change when it cools. For such samples, the following rule is observed: nitrogen porosity is greater than benzene porosity.

But the thermal expansion coefficient of many polymers is higher by one or two orders. For example, $\alpha = 4.5 \times 10^{-4}$ deg^{-1} for polystyrene, and $\alpha = 4 \times 10^{-4}$ deg^{-1} for cellulose. Thus, when they are cooled by 200°, the volume should decrease by 0.1 cm^3/g owing to thermal shrinkage. If the total volume of polymer pores is of the same order of magnitude, this means that it should decrease sharply on cooling. In this case nitrogen porosity, determined at —195 °C, will turn out to be less than benzene porosity determined at room temperature (Table 20.1). For such polymers, the method of low-temperature sorption of nitrogen vapours does not give a correct estimate of their porous structure.

TABLE 20.1. *Specific Surfaces of Some Polymers*

Polymer	Specific surface S_{sp}, m^2/g	
	according to nitrogen	according to organic substances
Polyethylene	2.8	0
Polytetrafluoroethylene	4.1	0
Copolymers of styrene with divinyl benzene	278.4	88.4
	423.8	94.2
Cellulose	9.0	42.1
Ethyl cellulose	17.2	73.1

4. Forced elastic recoverable deformations (p. 268) may develop in polymers which are in a solid state, under the action of high pressures. This may be revealed in mercury porosimetric measurements. In the case of uniformly porous polymers, when all the pores are filled up at practically the same pressure, the pore walls, experiencing pressure from both sides, may contract, i.e., they are "premoulded". When there are pores of various sizes, they are filled with mercury at different pressures. Under these conditions, the wall between two pores (one of which is filled with mercury while the other is still not filled) may become deformed under unilateral pressure, as a result of which the pores are

closed. There are indications of the possibility of the recoverable compression of polymers in the course of porosimetric measurements. On the other hand, it has been shown that the test of some polymers in a porosimeter does not cause a considerable change in their porosity.

20.4. METHODS OF FORMING POROUS STRUCTURE OF POLYMERS

Porosity is not an inherent property of a given substance. It is formed during the preparation of a sample, and one should know the laws of its formation so as to obtain materials of given porosity and also monolithic polymeric materials deprived of porosity.

There are several methods of obtaining porous materials, including porous polymers, which are used in polymer synthesis and in the moulding of finished articles.

1. **The thermal treatment of compact material.** This process is accompanied with the removal of volatile products or even water of crystallization from it. That is how porous activated charcoals or zeolites are obtained. When various polymers are thermally treated, highly porous coals are obtained [e.g., Sarans, coals which are products of pyrolysis of poly(vinylidene chloride)].

2. **The introduction of porophores** (substances producing porous structures) **into a polymer.** Under definite conditions, these substances decompose with the formation of gaseous products, which cause a polymer to bulge with the subsequent fixation of the porous structure formed.

3. **The saturation of a polymer with a gas** (usually nitrogen) **at high pressure** ($\sim$200 atm) **with the subsequent pressure drop.** In this case, pressure created inside a plate causes its bulging and the formation of pores. The dimensions of these pores depend on the plasticity of a material, i.e., on its compliance and on the conditions of the pressure drop. This is one of the techniques of obtaining spongy cellular rubbers, such as the Anazot sponge.

4. **The introduction of suspensions of organic or inorganic solids** with definite dimensions of particles into monomers with their subsequent removal from the prepared polymer.

5. **The conducting of polymer synthesis or the moulding of articles in the presence of a solvent with its subsequent removal.** Then, cavities of sufficiently large size that were occupied earlier by a solvent remain in a polymer. When a solvent is being removed (by drying) from swollen gels, a big role is played by shrinkage stresses, which cause shrinkage deformations and the "construction" of the structural framework, i.e., the shrinkage of the entire material. This was studied in detail by Rehbinder and Ostrikov. A body may contract by 8-20 times owing to shrinkage

stresses in the course of drying. Then, pore walls in porous bodies draw closer, and in some cases pores are completely closed.

The shrinkage stresses depend on the surface tension σ of a liquid and on the nature of a solid, on its ability to shrink. The substitution of a liquid having high σ for a liquid with low σ should cause a decrease in the contraction forces, a reduction in shrinkages, and, consequently, the formation of a more porous structure. From this viewpoint, a maximally developed porous structure of a body may be obtained at $\sigma = 0$, i.e., when liquid is removed under critical conditions; this removal is very difficult, but it was effected for several macroporous mineral sorbents.

Shrinkage phenomena are considerably affected by the nature of a body, its strength, rigidity and elasticity. These phenomena are practically absent in materials of the greatest rigidity (porous silicate glass, ceramics), and elastic polymers have the greatest reversible shrinkages. A very important regularity stems from this: to obtain a highly porous structure, the polymeric framework must be as little elastic as possible when the solvent is being removed. This is attained by introducing a large number of cross-links and choosing qualitatively poor solvents, which do not plasticize polymers (p. 557).

A polymer structure can be purposely loosened by swelling it in a good solvent and subsequently substituting the solvent with liquids which are poorer solvents with respect to a given polymer. Such a drying method is known as *inclusion.* It is used, for example, to obtain a looser structure of cellulose which is needed, say, for the technology of producing of acetatic fibres by continuous method. Cellulose may be allowed to swell in water, which is its plasticizer; consequently, the gel formed is elastic enough, and a more closely packed material is obtained owing to great shrinkage when water evaporates. But if water is substituted with methanol, and then the latter with pentane, the last liquid will occupy much space, which was formerly occupied by water. In the presence of pentane, the cellulose structure is more rigid; the liquid reacts poorly with cellulose, has a low boiling point, and therefore readily evaporates. A considerably looser porous structure then remains. A porous structure is always obtained when a solution of a polymer in a good solvent is poured into a precipitant.

A porous structure can be created by so-called *lyophilic drying.* This method consists in freezing a polymer solution to the temperature of liquid nitrogen and evacuating it at this temperature. The solvent is sublimed, while the frozen polymer structure changes comparatively little.

It follows that a porous polymer structure is obtained in the presence of a solvent. Polymerization or polycondensation in a

solution always causes the formation of a porous structure, and this is specially used in several cases for obtaining porous polymers of a three-dimensional network structure. Such a method can be used to obtain porous fibres and films.

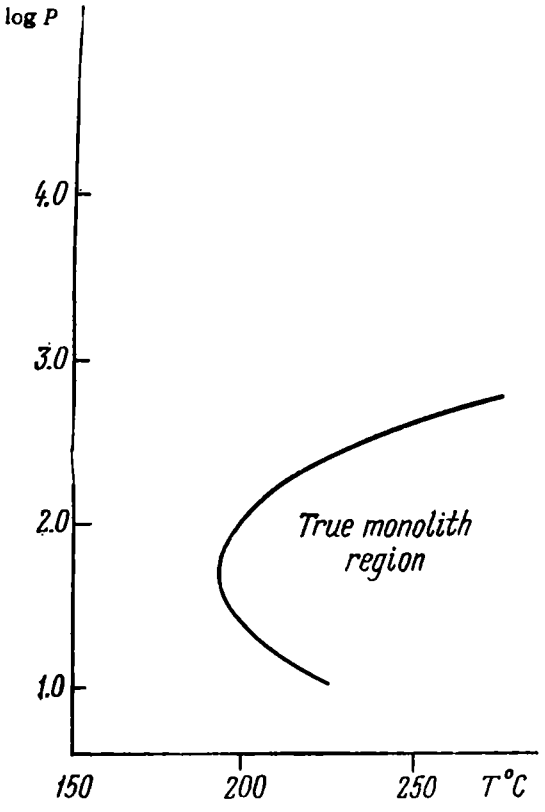


Fig. 20.2. Schematic representation of pressure and temperature effect on the obtaining of monolythic polymers

The degree of porosity depends on the quality of a solvent and on its thermodynamic affinity for a polymer, which may play a dual role.

On the one hand, the use of poor solvents should cause the "microprecipitation" of a polymer from a solution, i.e., the aggregation of macromolecules, and this leads to their closer packing. From this viewpoint, it may be expected that when polymers are being synthesized or moulded in the medium of poor solvents, packing density and porosity should be less than when they are being obtained in the medium of good solvents. This is observed in many cases. For example, polyurethane samples synthesized in the medium of poor solvents have a higher density than those synthesized in the medium of good solvents. Samples of the same polyarylate that are synthesized in the medium of poor solvents have lower porosity than those synthesized in the medium of good solvents.

On the other hand, poor solvents often poorly plasticize polymers, and the gels formed in the course of three-dimensional polymerization or polycondensation turn out to be less elastic than those formed in the medium of good solvents. Therefore, they have lower ability of undergoing shrinkage when the solvent is being removed: the structure of a dry three-dimensional polymer turns out to be more porous. As we have already seen, a more porous structure of cellulose is obtained by the inclusion method, i.e., by the substitution of good solvents for poor ones.

The methods of obtaining a porous structure of polymers were considered above. But it is often necessary to tackle a contrary task, i.e., the production of monolithic polymeric articles, which

n general are very difficult to obtain from solutions. Nonporous films may be obtained from a solution only by evaporating a solvent at high temperature, when macromolecules and supermolecular structures are sufficiently mobile. Therefore, monolithic polymer articles are obtained from melts at high temperature and high pressure. Table 20.2 clearly shows how the apparent density

TABLE 20.2. *Density and Porosity of Polyarylate* Ф-1 *Depending on Compression Pressure*

Compression pressure	Density, g/cm³	
	apparent, d_{ap}	true, d_{true}
0	0.920	1.300
10	1.100	1.300
500	1.250	1.300
3125	1.300	1.300

(p. 608) of polyarylate grows with an increase in pressure and approaches the true density of a monolithic material. However, as Arzhakov, Shtarkman and their coworkers have shown, a polymer in the state of a true monolith can be obtained only in a definite range of temperatures and pressures, which are characteristic of each polymer. By true monolith, the authors imply the state of a polymer when inner stress, which originates in the course of compression of a powdery mass, has time to relax practically completely. Figure 20.2 gives the true monolith range of poly(methyl methacrylate).

20.5. POROUS STRUCTURE OF POLYMERS. CLASSIFICATION OF POLYMER SORBENTS

The structure of polymer bodies, especially crystalline ones, is dealt with in many works and it is considered in Chap. 5. However, the ordering of macromolecules and morphological formations are considered in detail, while little space is devoted to the porous structure of polymers, although it is an important question.

The parameters of a porous structure are estimated for many polymers, and Rodgers attempted to classify polymer sorbents according to the type of sorption isotherms which he connected with the mechanism of surface covering. Concepts of the role of a porosity of a sorbent in adsorption processes evolved simultaneously with theories which connected adsorption processes only with the surface. The most fruitful are Dubinin's classification of sorbents according to the pore size and Kiselev's classification, in which the

type of isotherms is connected not only with the size of a surface, but also with the pore size. These classifications can be used also for polymer sorbents.

An analysis of more than 200 isotherms of "inert" vapours (which do not cause swelling) on various polymers have made it possible to divide them into four basic types, which are represented in Fig. 20.3.

The first type of sorbents are *nonporous sorbents* (Fig. 20.3*a*), which are characterized by S-shaped isotherms without sorption

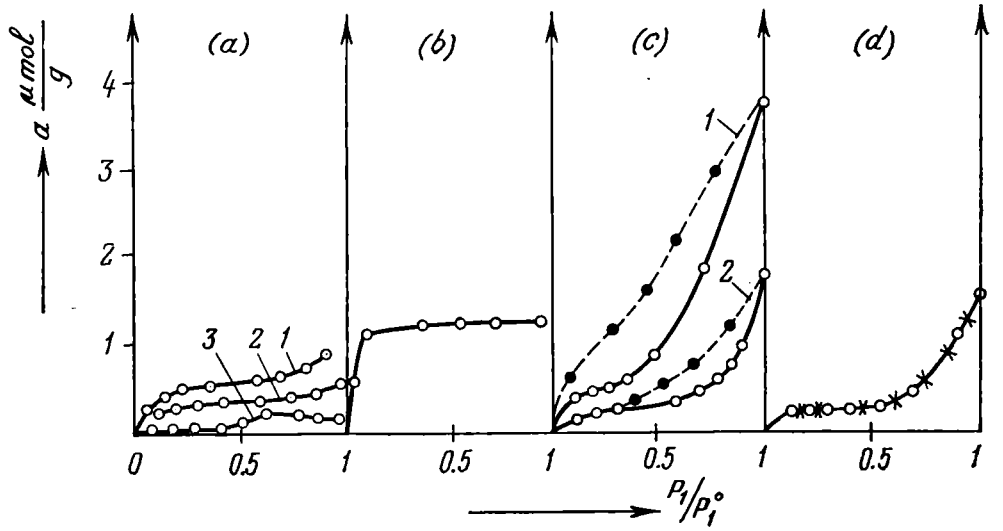


Fig. 20.3. Sorption isotherms of "inert" liquids' vapours on polymers: *a*—nonporous: *1*—PVC: *2*—polyvinylidene chloride; *3*—PS; *b*—microporous; *c*—sorbents with transitional pores: *1*—copolymer of styrene and divinylbenzene synthesized in solvent medium; *2*—polyacrylate; *d*—macroporous (○—Styroflex film; ×—macroporous PS film)

hysteresis and a small amount of the maximally absorbed sorbate. Such isotherms are observed for several crystalline polymers [poly(vinyl alcohol), poly(vinylidene chloride), etc.] and some closely-packed glassy polymers [bulk poly(methyl methacrylate) and polystyrene]. Crystalline polyethylene in the region of small relative vapour pressures practically does not sorb the vapours of "inert" sorbates, such as methanol, and inconsiderable sorption is observed only at higher values of P_1/P_1^0. Such polymers are characterized practically by a zero value of the total pore volume ($W_0 \cong 0$) and very small values of the specific surface ($S_{sp} = 1$ to 7 m^2/g).

The second type of polymer sorbents is *microporous* or *uniformly fine-porous sorbents* which have a pore radius of up to 16 Å and are characterized by the Γ-shaped isotherms (Fig. 20.3*b*); the shape of these isotherms is determined not by the saturation of a surface by sorbate molecules, but by the fact that a large

number of molecules cannot penetrate into fine pores. The concept of the specific surface for microporous sorbents has no physical meaning whatsoever, while the total volume of the pores of microporous polymers may attain values of 0.5 cm^3/g. As we may see from Fig. 20.3*b*, the steepness of the initial segment of the isotherms of sorption on polymeric microporous sorbents is considerably less than, say, that of coals obtained by carbonizing poly(vinylidene chloride) (Sarans) or zeolytes. This is quite understandable, because a large number of fine pores of the latter originate as a result of the removal of HCl or water from them.

The third type of polymer sorbents are *sorbents having transitional pores*, whose radius is in the range of 16 Å to 1000-2000 Å. Such polymers are characterized by S-shaped isotherms with a large sorption hysteresis (Fig. 20.3*c*). They are capable of absorbing large amounts of a sorbate and have values of W_0 and S_{sp} that attain 0.8 cm^3/g and 700-900 m^2/g, respectively.

The fourth type are *macroporous polymer sorbents* having a pore radius of hundreds of thousands of angstroms. According to Dubinin, the inner surface of such enormous voids acts as an outer surface, and their sorption isotherms are the same as those of nonporous sorbents. Indeed, we can see from Fig. 20.3*d* that the isotherms of sorption of methanol vapours of a nonporous film of Styroflex and a specially prepared macroporous sample of polystyrene, which has cracks, completely coincide.

Real polymers often cannot be related to a definite type of sorbents. It is especially difficult to obtain uniformly fine-pore polymer sorbents. They are sometimes known as isoporous sorbents, and are obtained not by the reactions of polymerization or polycondensation, but by the crosslinking of the already prepared polymers with the aid of some substances, for example, by the crosslinking of polystyrene with *para*-xylilene chloride.

Most amorphous polymers are, by their structure, sorbents, which A. V. Kiselev calls sorbents of a mixed type. They are characterized by diffused S-shaped isotherms (Fig. 20.3*d*) and have pores of the most diverse sizes (from units to hundreds of thousands of angstroms).

The presence of such enormous pores apparently attests to distances not between macromolecules, but between larger supermolecular structures, while the pore walls may be packed very closely. Thus, amorphous polymers are very inhomogeneous by their structure, and this is sometimes observed also for some crystalline polymers. For example, large-sized pores, apparently formed between crystallites, have been detected in isotactic polystyrene.

The total pore volume determined from sorption data does not reflect the entire pore volume, because the volume of very small

and very large pores cannot be estimated by the sorption method (p. 595). Therefore, the concept of the maximum pore volume W_0^{max} was introduced; it implies to the volume of all the pores into which molecules of any dimensions may penetrate. Its value can be calculated by imagining a hypothetical case when a polymer has pores of different sizes, and their walls have the packing of an ideal crystal or an ideal monolithic amorphous substance. Then

$$W_0^{max} = V_T - V_{id.\,cr} \quad \text{or} \quad W_0^{max} = V_T - V_{monol} \qquad (20.11)$$

The quantity W_0^{max} can also be calculated by the equation

$$W_0^{max} = \frac{1}{d_{ap}} - \frac{1}{d_{true}} \qquad (20.12)$$

where d_{ap} and d_{true} = apparent and true densities, respectively.

It follows that W_0^{max} is a porosity factor, which is calculated for mineral and polymeric sorbents.

Apparent density d_{ap} is the density of a body at a given temperature with regard to the pores in it. For particles of regular geometric form, it is determined on the basis of the geometric dimensions of a body and its mass. For friable bodies with particles of irregular shape, d_{ap} is determined pycnometrically or dilatometrically by means of liquids which practically do not wet the surface of a given body and, consequently, do not penetrate into its pores. Mercury (without pressure) is mainly used for this purpose.

True density d_{true} implies the density of the thick part of a sample or the pore "walls". It is also determined pycnometrically or by means of gradient tubes with the use of liquids which wet the surface of a body well and penetrate into pores.

The values of d_{ap} and d_{true}, determined pycnometrically, may depend on the size of molecules of the liquids used. Therefore, it would be correct to take, as the "true" density of a polymer, its density in the state of an ideal crystal or a true monolithic amorphous polymer.

The densities of bodies determined in the medium of liquids which wet and do not wet their surface may greatly differ from one another. This fact is known well to researchers studying porous mineral sorbents. Unfortunately, articles, textbooks and monographs on polymers often do not indicate the conditions under which given values of density were determined; they should be indicated, because many polymers have a porous structure.

As we have seen in Chap. 6, in addition to the parameters of the porous structure of bodies, there are other concepts which concern the empty space in bodies, i.e., the free volume and the

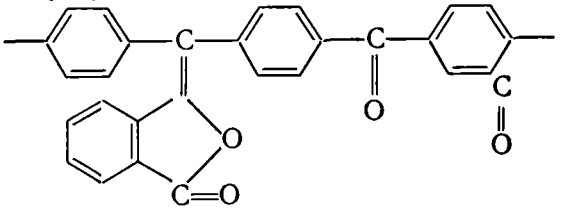
packing factor. It is of certain interest to compare them with one another.

If, according to Hildebrand and Bondi, the empty or free volume of a body V_E implies the difference between its volume at a given temperature and the proper volume of molecules, then the value of V_E, calculated for crystals by Eq. (6.10), will be of the order of 0.25-0.30 cm^3/g. Thus, even ideal crystals have a rather large free volume. But they are, as a rule, nonporous sorbents, i.e., even the smallest molecules cannot penetrate into the ultramicroscopic voids of crystalline bodies. Diffusion in the lattice of such crystals as NaCl is possible only if they have defects.

If Eq. (6.10) is formally used for calculating the empty or free volume of a porous polymer, we will obtain very large values which attain 2-4 cm^3/g. Apparently, this empty volume includes the total pore volume W_0^{max}, which is always less than V_E.

Table 20.3 gives the values of V_E, W_0^{max} and the packing factors of some polymers.

TABLE 20.3. *Values of Densities, Free Volume, Maximum Pore Volume and the Packing Factor of Some Polymers*

Polymer	Density d_a, g/cm^3	V_E		W_0^{max}, cm^3/g	Packing factor K
		cm^3/g	cm^3/mole of a unit		
Polyethylene (PE) (100 per cent degree of crystallinity)	1.00	0.26	7.2	~0	0.740
Polyisobutylene	0.912	0.35	10.6	~0	0.678
Poly(vinyl acetate) (PVA)	1.189	0.28	24.1	~0	0.665
Polystyrene (PS)	1.05	0.32	33.3	0.06	0.666
Polyarylate 	0.90	0.82	367.3	0.58	0.477

It follows from the table that W_0^{max} is practically equal to zero for the first three polymers. Thus, the empty volume V_E is the volume of ultramicroscopic voids, which exist in elastic, glassy or crystalline polymers. However, these polymers are distinguished by packing density, and this becomes especially clear when the values of V_E calculated per mole of a unit are compared. Apparently, crystalline PE is the most densely packed

polymer, and then comes polyisobutylene and PVA. Polystyrene is a more loosely packed polymer; the value of V_E calculated per mole of its unit is 33.3 cm^3.

Data given in the table show that the quantity V_E, cm^3/mole, is a more sensitive parameter which characterizes the packing density of macromolecules of polymers than K.

Polyarylates have very high values of W_0^{max} and V_E, like other polymers synthesized in solutions. The values of K formally calculated by Eq. (6.14) are far smaller than those of nonporous polymers. Such low values of K indicate the loose packing of supermolecular structural formations, i.e., polymer porosity. Thus, "porous structure" and "loose molecular packing" are inadequate concepts.

20.6. MECHANISM OF SORPTION OF LOW-MOLECULAR SUBSTANCES BY POLYMERS

The mechanism of sorption of low-molecular substances on polymers is very intricate. It depends on the phase state and the physical state of a polymer, its porous structure, chemical composition, chain flexibility, interchain interaction and its thermodynamic affinity for a sorbate. Depending on the value of the latter, a polymer may turn out to be perturbed to a different extent in the course of sorption, and the sorption mechanism will be different.

20.6.1. Mechanism of Sorption of Inert Sorbates on Polymers

At very low thermodynamic affinity of the vapours being sorbed for a polymer, the latter is perturbed to a small extent, and its volume swelling is practically null. In this case, the sorption mechanism practically does not differ at all from that on mineral sorbents.

For example, nonporous crystalline, glassy or elastic polymers interact with "inert" sorbates solely by their outer surface, which is very small. Only physical adsorption is observed when there is no chemical interaction between a polymer and a sorbate (p. 593).

The interacting centres of micropore sorbents permeate their entire volume. Therefore, the mechanism of volume pore filling is observed for microporous polymer sorbents; this filling may be regarded as a process of dissolution of an "inert" gas or vapour in the volume of a body.

For sorbents having transitional pores, there is the mechanism of the layer-by-layer filling of pore walls, the merging of the mul-

tilayers formed and capillary condensation, as a result of which sorption hysteresis is observed.

As regards macropore sorbents, multilayers do not merge because the pore walls are far away. Therefore, there is no capillary condensation, and only physical adsorption is observed. In this case, the surface of very large pores acts as an outer surface; it is usually small, as a result of which adsorption on macropore sorbents does not differ from that on nonporous sorbents (Fig. 20.3*d*).

20.6.2. Mechanism of Sorption of Noninert Vapours on Polymers

When the thermodynamic affinity of a sorbate for a polymer is sufficiently high, the specific features of the latter begin to be exhibited: a polymer swells in volume and changes its structure. In this case, a big role is played by the flexibility of polymer chains, the density of their packing, interchain interaction and the physical state of the sorbing polymer.

In the case of close packing of macromolecules and supermolecular structures, when porosity is absent, the sorption of noninert vapours should be regarded as a process of their dissolution in the entire volume of a body or in the "matrix" of a polymer. The mechanism of the dissolution above the glass-transition temperature T_g differs from that below this temperature.

At $T > T_g$, when the sorbing polymer is in a rubber-like state, sorption is, in essence, a swelling process whose mechanism consists in the exchange of places of sorbate molecules and units, or segments, of flexible macromolecules (p. 338). When a polymer chain is sufficiently flexible, such rearrangements are possible from the very first portions of an absorbed gas or vapour, i.e., from the lowest values of its pressure P_1. Therefore, the isotherms of sorption on elastomers always have the shape of curves concave toward the abscissa axis in the entire range of P_1/P_1^0 (Fig. 20.4*a*). The poorer is a solvent thermodynamically, the lower is the sorption isotherm, and the nonsolvent is not absorbed by densely packed nonporous elastomers. The sorption or swelling as a whole depends on the affinity of a solvent for a polymer and on the chain flexibility of the latter. When different polymers have the same chain flexibility, the sorption of the same substance on them is expressed by a single curve.

At $T < T_g$, segmental motion is practically not realized. Therefore, it is difficult for vapour molecules to exchange places with units of a polymer chain, and the former can penetrate only into the voids which exist in a polymer; but closely packed polymers have a small number of voids. Therefore, in the initial region of

P_1/P_1^0, such polymer sorbents sorb very little. The amount of the substance sorbed by them is often beyond the sensibility limit of a sorption method. Sorption becomes noticeable at definite values of P_1, when a system passes over to an elastic state and the exchange of places between sorbate molecules and chain units, i.e., polymer swelling, is possible. This mechanism is exhibited in

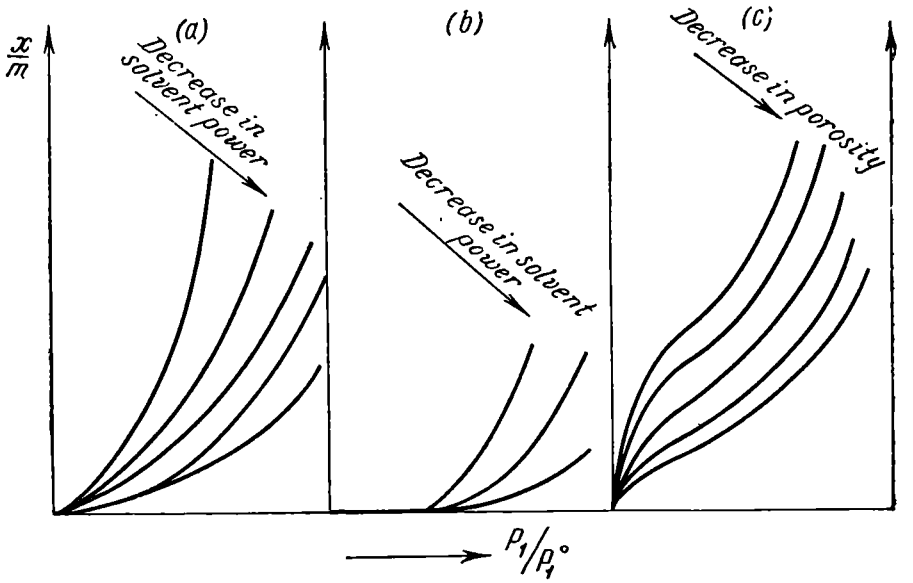


Fig. 20.4. Sorption isotherms of noninert liquids' vapours on polymers: *a*—highly elastic; *b*—glassy, densely packed; *c*—glassy, porous

sorption isotherms, whose typical shape is given in Fig. 20.4*b*. It is characteristic of sorption on densely packed spatially cross-linked glassy polymers.

A more complex sorption mechanism is observed for porous, loosely packed glassy polymers; the isotherms of sorption of noninert sorbates on them, like those of inert ones, are expressed by S-shaped curves with the initial segment concave up (Fig. 20.4*c*). This segment corresponds to the glassy state of a polymer-sorbate system, while the inflection point of the curve corresponds to the transition of the system at the experiment temperature from a glassy to a rubber-like state. Above this point, i.e., at high values of P_1/P_1^0, sorption occurs according to the mechanism which was described earlier and is characteristic of elastomers. At low values of P_1/P_1^0, the processes of the physical adsorption of a sorbate in the pores of a sorbent and the swelling of the latter occur simultaneously, and it is impossible to separate them.

Since these two processes occur simultaneously, sorption of the same substance on polymer samples having diverse porous structures may greatly differ at low values of P_1/P_1^0 (Fig. 20.5).

A very important conclusion is drawn from these data: the thermodynamic affinity of a solvent for a polymer depends not

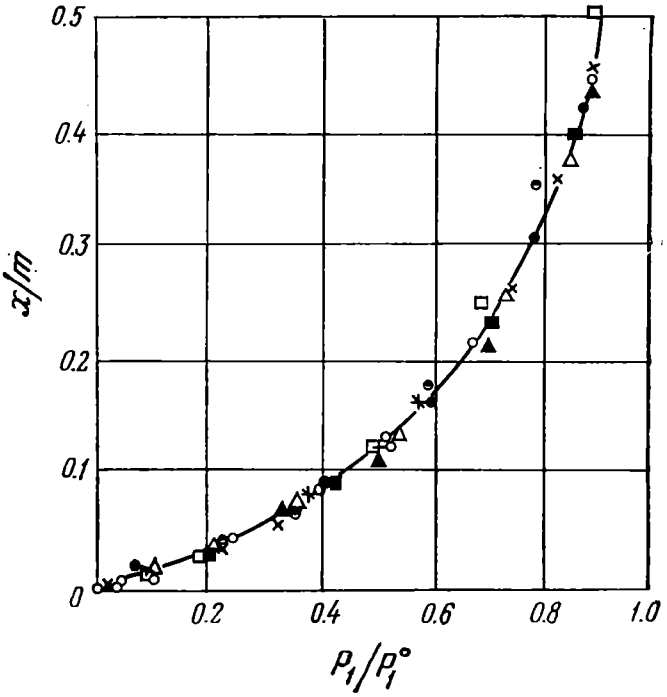


Fig. 20.5. Sorption isotherms of *n*-hexane on rubber-like polymers: ○—НК; ×—СКБ; ▲—СКБМ; ■—high-molecular fracture of СКБМ; ◓—СК-1; ●—СК-2; *—СК-3

only on the chemical nature of the latter, but also on its porous structure. Indeed, we will obtain different values when we calculate by such isotherms $\Delta\mu_1$ (p. 428) or the parameter of interaction χ_1 (p. 429). The value of χ_1 for a nonporous sample grows, according to the theory with an increase in concentration, while for a porous sample it diminishes and becomes negative. The curves coincide at definite concentrations. This fact was first observed by Moore for solutions of cellulose ethers; this is apparently due to the loose packing and porous structure of the latter.

20.7. ION-EXCHANGE RESINS

Ion-exchange resins, or ionites, are polymer sorbents which have a three-dimensional reticular structure and contain ionogenic groups that are capable of dissociation and ion exchange with the surrounding medium. Ion-exchange resins do not dissolve in the

medium from which they absorb ions, and therefore they should have a reticular structure. They are often called *crosslinked polyelectrolytes.*

The former is the product of condensation of phenol and formaldehyde, and the latter is the product of polymerization of styrene and divinyl benzene, which is a crosslinking agent. The sulphogroups, $-SO_3H$, are introduced into them by sulphonation; in an aqueous medium, these groups dissociate as follows:

$$-SO_3H \rightleftarrows -SO_3^- + H^+$$

The negative SO_3^- ions form part of the polymer and remain fixed, while the mobile positive hydrogen ions form a diffuse shell around the negatively charged surface of the crosslinked polymer. These hydrogen ions are capable of exchanging for the positive ions contained in the solution.

Ionogenic groups can be introduced into spatially crosslinked polymers or copolymers by means of reactions of chloromethylation, phosphorylation and other polymer analogous transformations. In some cases, they are contained in monomer molecules themselves which are starting material for ionites. Other substances may also be crosslinking agents. Therefore, there is a large number of diverse ion-exchange resins.

Like mineral sorbents, ion-exchange resins fall into cation and anion exchangers. *Cation exchangers* are insoluble crosslinked polyacids or their salts, consisting of a fixed negative macroion and small mobile positive ions capable of exchange. *Anion exchangers* are insoluble crosslinked polybases or their salts, consisting of a fixed positive macroion and small mobile negative ions capable of exchange. Ion-exchange resins may contain ionogenic groups of one type, i.e., groups of equal acidity or basicity, or ionogenic groups of different types, i.e., groups of different acidity and basicity.

Monofunctional ion-exchange resins are resins containing one definite species of functional groups, e.g., sulpho groups, carboxyl groups, phosphoric acid residues, oxyphenyl groups, etc. Of polyfunctional ion-exchange resins we may mention products containing sulpho and carboxyl groups, sulpho and oxyphenyl groups, etc. All the resins enumerated are cation exchangers.

Monofunctional anion exchangers may contain, as their ionogenic groups, tertiary, secondary, or primary amino groups. These are quaternary ammonium and sulphonium polybases.

With respect to degree of ionization, ion exchangers are classified into strongly acid, weakly acid, strongly basic, and weakly basic exchangers.

Strongly acid cation exchangers enter into the reaction of ion exchange with the salts of acids in neutral and acidic aqueous

solution. In neutral solution weakly acid cation exchangers are capable of ion exchange only with cations of the salts of weak acids, the completeness of exchange increasing with increasing pH of the solution. Such are carboxyl and oxyphenil ion exchangers.

Strongly basic anion exchangers are capable of ion exchange in neutral and weakly alkaline solutions (quaternary ammonium bases). Weakly basic anion exchangers enter into ion exchange only in acid solution, the completeness of exchange increasing

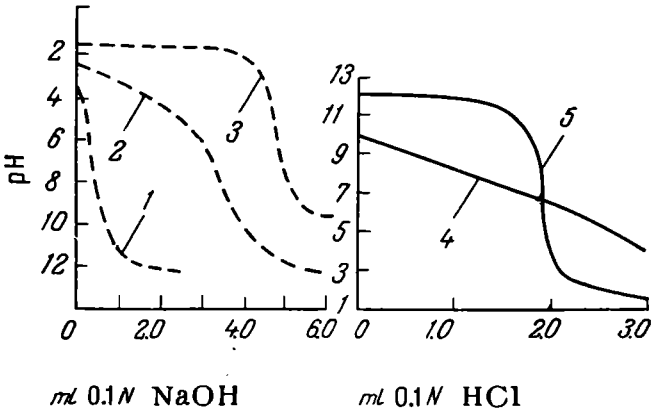


Fig. 20.6. Potentiometric titration curves of ion exchangers:
1—weakly acidic; *2*—medium acidic; *3*—strongly acidic; *4*—weakly basic; *5*—strongly basic

with decreasing pH of the solution (resins containing primary, secondary, and tertiary amino groups).

There are ion exchangers possessing the property of *ampholytes*. They contain both acidic and basic groups, e.g., amino and sulpho groups, amino and carboxyl groups.

Cation-exchange resins can be used in the hydrogen form (H-form) or in the salt form (Na-form). In the former case the hydrogen ions — and in the latter, the metal ions — of the ionogenic groups of the sorbent exchange for the cations of the dissolved electrolyte.

Anion-exchange resins can be used in the form of bases or salts.

The content of ionogenic groups in the resin is determined by potentiometric titration. Different ionogenic groups give different shapes of curves for pH versus content of NaOH or HCl in the solution (Fig. 20.6).

The process of exchange between the electrolyte ion and the mobile sorbent ion passes through the following stages:

(1) movement of the displacing ion from the bulk of solution to the sorbent surface;

(2) movement of the displacing ion inside the sorbent to the point of exchange;

(3) chemical exchange reactions, i.e., the ion exchange reaction proper;

(4) movement of the displaced ion inside the sorbent from the point of exchange to its surface;

(5) movement of the displaced ion from the sorbent surface into the bulk of the solution.

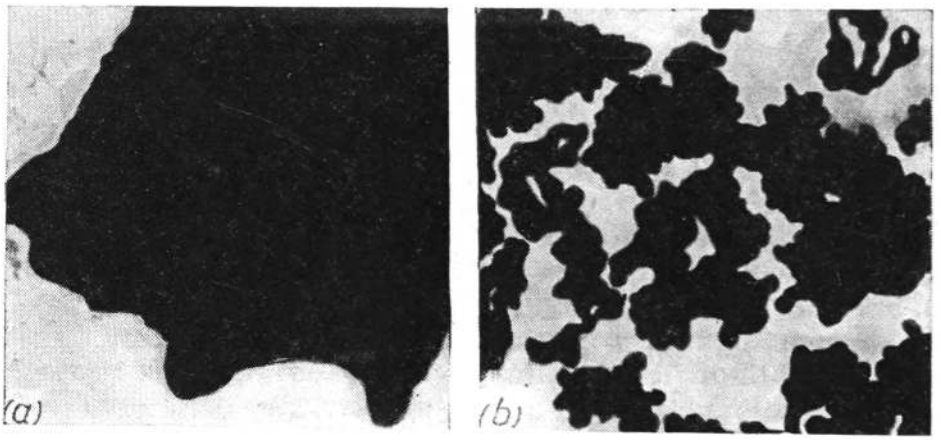


Fig. 20.7. Ion-exchange resins:
a — standart; *b* — macroporous

The kinetics of these processes is determined by the value of the diffusivities of ions, and this is connected with their dimensions and the resistance of a medium. The magnitude of sorption and the capacity of the ionite depend on the affinity of the ion for a resin, the density of a network, the degree of swelling and porosity of the ionite.

Ion-exchange resins are divided into "standard" or "gel" ones and macroporous ones according to the technique of obtaining them (Fig. 20.7*a*, *b*).

20.7.1. Gel Ion-Exchange Resins

Gel ionites are obtained on the basis of spatially crosslinked polymers or copolymers, whose synthesis is effected in a bulk (p. 53). Copolymers into which ionogenic groups are introduced are known as ionite "skeletons" or "frameworks".

The specific surface and total volume of pores of bulk skeletons and ionites prepared on their basis are very small. For example, for the gel ionite synthesized in the presence of 2 per cent divinyl benzene, $W_0 = 0.004$ cm^3/g and $S_{sp} = 0.1$ m^2/g. These values are 1-3 orders lower than those of many polymers (Tables 20.1 and 20.2).

20.7.2. Standard or Gel Ion-Exchange Resins

The exchange capacity of an ordinary or standard ion-exchange resin depends not only on the ability of its mobile ions to exchange with the ions of the solution, but also on the ability of the displacing ions to penetrate into the resin. When mineral sorbents are used, the possibility of ions penetrating into it depends on the ratio of the porosity of a sorbent and the size of the displacing ion. With small pores and large electrolyte ions no ion exchange will occur.

By analogy with mineral sorbents one also uses the term *porosity* in application to ion-exchange resins.

The porosity of ion-exchange resins can be estimated by sorption of the vapours of inert liquids or by low-temperature sorption of nitrogen vapours (p. 610). These methods were used for estimating the porosity of what is known as *standard ion exchangers*, i.e., ion-exchange resins produced by ordinary methods of copolymerization of styrene or other monomers with different cross-linking agents, e.g., with divinylbenzene. These investigations have shown that the specific surface area and total pore volume of such ion exchangers are very small. Thus, the total pore volume of an ion exchanger synthesized in the presence of 2 per cent divinylbenzene is 0.004 cm^3/g, and in the presence of 16 per cent divinylbenzene, 0.001 cm^3/g. These values are one decimal order smaller than the total pore volume values of linear polymers (p. 596) and two orders smaller than the total pore volume of good porous coals. The specific surface area of such ion exchangers amounts to about 0.1 m^2/g, whereas for mineral sorbents it is 600-800 m^2/g.

Obviously, the high absorptive power of standard ionites is not connected with their porosity. Such ion exchangers can absorb only small ions. Larger ions, such as those of terramycin, penicillin, and other antibiotics can be taken up by them only from media in which they swell. In the latter case there is a direct dependence between the absorptive power of the ion-exchange resin and its ability to swell in the medium from which it sorbs the ions. This is clearly illustrated by Fig. 20.8.

Sorption of ions occurs mostly from aqueous solution, and therefore the ability of a resin to swell depends primarily on the degree of hydration of its ionogenic groups, which determines the affinity of the resin for water. The higher the degree of hydration, the more will the resin swell. The degree of swelling is also affected by the species of electrolyte ions in the solution. If the ability of the displacing ions to hydrate is lower than that of those being displaced, addition of a moist swelling ion exchanger to a concentrated solution of a salt or an acid will cause the ion

exchanger to contract as a result of passage of part of the water into the solution.

The degree of swelling of an ion-exchange resin also depends on the number of crosslinks in the polymer. The larger the number of crosslinks, the lower the degree of swelling. Despite the obviousness of this relationship, its quantitative characteristic has

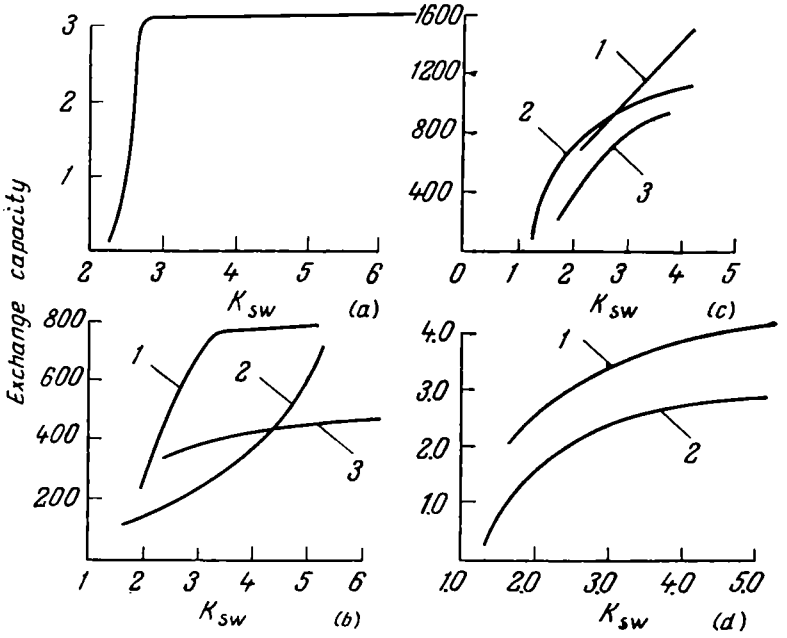


Fig. 20.8. Exchange capacity of ion exchangers with different swelling coefficient (K_{sw}) with respect to antibiotics:

a—exchange capacity of amberlite IRA-400 anion exchanger with respect to penicillin; *b*—exchange capacity of carboxyl cation exchangers with respect to streptomycin: *1*—КФУ; *2*—КМТ; *3*—КМД; *c*—exchange capacity of sulpho resins with respect to aureomycin: *1*—КФУ; *2*—КНФ; *3*—ССФ; *d*—exchange capacity of sulpho resins with respect to terramycin: *1*—ССФ; *2*—СБС

not been established, because the exact number of crosslinks is usually unknown (it is difficult to determine what part of the substance has reacted, though the amount of crosslinking agent added to the copolymerization is known).

In the process of swelling the ion-exchange resin alters its structure considerably, i.e., behaves like a typical nonrigid sorbent, and therefore with respect to swollen ion-exchange resins the terms "microporosity" and "intramolecular porosity" do not apply at all. During sorption on ion-exchange resins the polymer swells, i.e., the resin is a solution of a micromolecular liquid in a crosslinked polymer and its absorptive power can best be estimated from its degree of swelling (Chap. 13). The degree of swelling gives a quantitative estimate of the total volume occupied by the low-molecular liquid in the swollen polymer. This volume has

nothing in common with the total pore volume, being hundreds of times larger than the latter. Swelling always results in a decrease of strength of a polymer and hence reduces the service life of the ion exchanger.

With respect to ion-exchange resins the term "permeability" can be used, but this term then has a specific meaning.

The process of exchange between the electrolyte ion and the mobile sorbent ion passes through the following stages

(1) movement of the displacing ion from the bulk of the solution to the sorbent surface;

(2) movement of the displacing ion inside the sorbent to the point of exchange;

(3) chemical exchange reactions, i.e., the ion exchange reaction proper;

(4) movement of the displaced ion inside the sorbent from the point of exchange to its surface;

(5) movement of the displaced ion from the sorbent surface into the bulk of the solution.

The permeability of an ion-exchange resin is determined by the second stage of the process, which depends on the ion sorption value and the diffusion coefficient, the latter depending, in its turn, on the size of the diffusing ion and the resistance of the medium. The diffusion coefficients of the displaced and displacing ions, as well as the first and fifth stages of the process, determine the kinetics of ion exchange. The amount of ions sorbed by the resin depends on the affinity of the ion for the resin and the degree of swelling of the latter, and determines the dynamics and statics of ion exchange. Thus, the permeability of an ion-exchange resin depends on the statics and kinetics of ion exchange, both of the latter depending on the degree of swelling.

The swelling of ion-exchange resins determines to a considerable extent the selectivity of the latter. Strongly swelling ion exchangers take up ions of all sizes well, i.e., their selectivity is very low. Weakly swelling ion exchangers possess a high capacity for smaller ions and a low capacity for larger ones. This is the basic principle of the method of *ion-exchange sieves*, by means of which like-charged ions of different sizes can be separated. For example, by using weakly swelling ion exchangers metal ions can be separated from ions of macromolecular compounds, such as proteins, which are not practically sorbed. Complete demineralization of streptomycin is accomplished by means of ion-exchange sieves. Anions of different sizes can be separated in a similar way.

By using an array of ion exchangers of gradating degree of swelling, ions of comparatively close sizes can be separated. For instance, insulin has been separated in this way from other macromolecular organic compounds.

Very large ions can be sorbed only by strongly swelling ion-exchange resins, sorption in this case occurring throughout the entire mass of sorbent. A low degree of swelling of the ion exchanger and closeness of the ionogenic groups in the resin (part of these groups are then blocked by large ions and do not participate in the exchange reaction) lower the sorbability of organic ions. To increase the sorbability of very large ions, resins should be used with a decreased total exchange capacity (e.g., with respect to sodium ion), and with a high degree of swelling. For this purpose it is necessary for the resin to contain a sufficient amount of hydroxyl groups, which increase the degree of swelling, and for ionogenic groups to be arranged comparatively rarely. These requirements are met, for example, by carboxyphenol-formaldehyde resins.

20.7.3. Macroporous Ion-Exchange Resins

Workers in the field of synthesis of ion-exchange resins have long been trying to prepare sorbents close in porosity to the best grades of activated charcoals. Attempts to do this by decreasing the crosslink density in the "skeleton" of the copolymer and by using other monomers were unsuccessful. Methods involving a change in copolymerization technique and in structure of the ion exchanger gave better results.

At present methods of producing macroporous ion exchangers or, to be more exact, their macroporous "skeletons", have been outlined and are under development. One of these consists in copolymerizing the monomers in the presence of a blowing agent, i.e., a substance that decomposes on heating, evolving gaseous products which cause the network formed to expand. However, the main method of producing macroporous resins is by copolymerization in the presence of a third component, which does not participate in the reaction and is a good solvent for a monomer and a poor solvent for a polymer. The resulting copolymer should swell in these substances. The diluents used in the copolymerization of styrene with divinylbenzene, for instance, are *n*-heptane, isooctane, higher alcohols. After completion of the copolymerization, which is carried out, as a rule, in aqueous solution in the presence of an emulsifier, the diluent, now contained in the swollen copolymer, is removed by distillation with steam. This leaves pores of sufficiently large size in the copolymer.

Numerous investigations have shown that the structure and properties of the resulting copolymers differ from those of the "skeleton" of standard ion exchangers. Standard copolymers are colourless, transparent, and glassy; the new ion-exchange resins, known as *macroporous*, or *large crosslinked resins*, are opaque,

milk-white in colour, and possess decreased density, a low bulk mass, improved kinetic and mechanical properties, and high chemical resistance.

Detailed investigations of the porosity of the new type of ion exchangers revealed that their specific surface area and total pore volume depend on the amount of crosslinking agent and diluent used in the synthesis. Another factor of great importance is the purity of a monomer, particularly, divinylbenzene. The *m*-divinylbenzene contained in the commercial product has a lower reactivity than *p*-divinylbenzene, and therefore the crosslink density of the copolymer synthesized in the presence of commercial divinylbenzene is lower than expected. Figure 20.9 presents experimental data on the dependence of the specific surface area of styrene/*p*-divinylbenzene copolymers produced in the presence of various amounts of *n*-heptane, on the content of crosslinking agent. It follows from the figure that even if the copolymer is synthesized in the absence of a diluent, its specific surface area increases only slightly when the content of divinylbenzene is large.

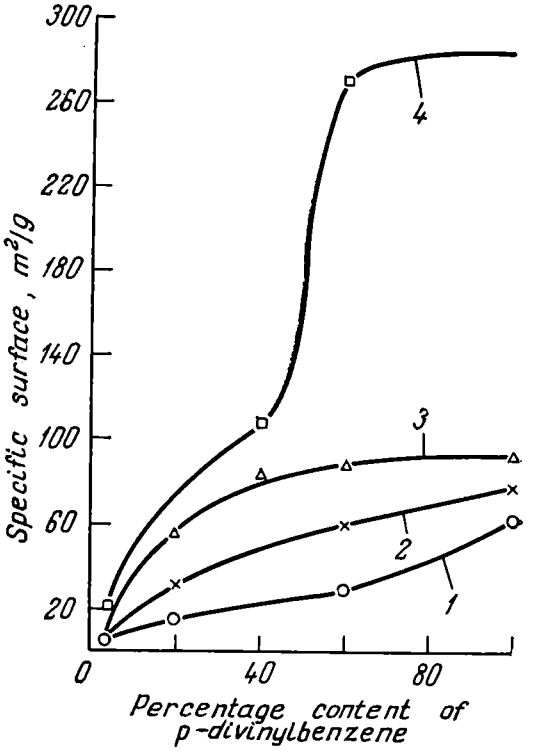


Fig. 20.9 Dependence of specific surface area of styrene/*n*-divinylbenzene copolymers on divinylbenzene content:

1—synthesized in the absence of diluent; *2*—30 per cent *n*-heptane; *3*—70 per cent *n*-heptane; *4*—100 per cent *n*-heptane

The content of crosslinking agent has an especially sharp effect on the porosity of a copolymer when the amount of the diluent is increased. If the specific surface area is between 10 and 100 m^2/g, the same value of this quantity can be obtained by synthesizing with a larger amount of *n*-heptane and a smaller amount of divinylbenzene or, vice versa, with a smaller amount of *n*-heptane and a larger amount of divinylbenzene. This is illustrated vividly by Fig. 20.10. A developed specific surface area can however be obtained only in the presence of large amounts of a diluent and a crosslinking agent. Table 20.4 lists the specific surface areas and total pore volumes of some copolymers, determined by organic vapour and nitrogen sorption. Analysis of the

data of this table shows that in some cases the nitrogen porosity is anomalously lower than the method porosity. This is observed in copolymers of comparatively low porosity, which evidently become greatly compacted on cooling. But in the case of rigid copolymers with a developed specific surface area, the slight compac-

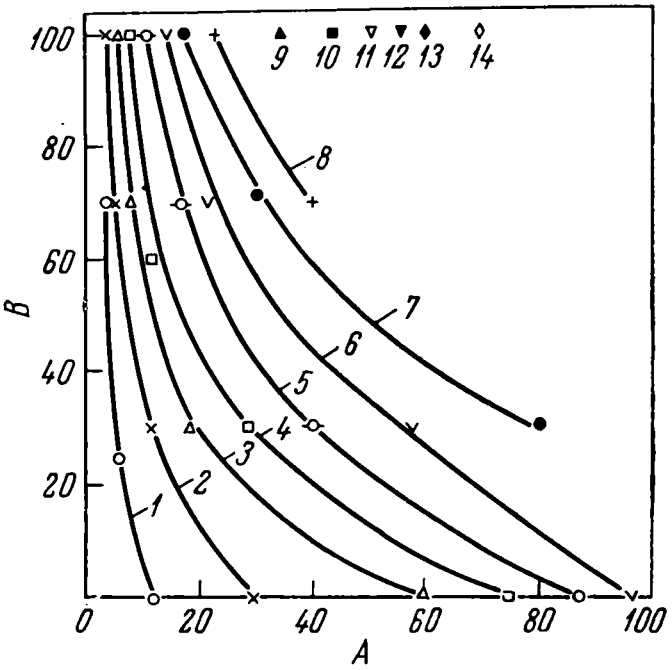


Fig. 20.10. Dependence of specific surface area of styrene/*n*-divinylbenzene copolymers on divinylbenzene and *n*-heptane content (*A* — content of *n*-divinylbenzene in monomer mixture; *B* — amount of *n*-heptane added, per cent of monomer mixture):

1—S_{sp}=10 m²/g; *2*—20 m²/g; *3*—30 m²/g; *4*—40 m²/g; *5*—50 m²/g; *6*—60 m²/g; *7*—70 m²/g; *8*—80 m²/g; *9*—100 m²/g; *10*—120 m²/g; *11*—200 m²/g; *12*—250 m²/g; *13*—270 m²/g; *14*—280 m²/g

tion caused by cooling is inessential and their nitrogen porosity is higher than their methanol porosity.

At present macroporous ion exchangers have been synthesized with a nitrogen specific surface area of approximately 900 m²/g, i.e., approaching that of the best grades of activated charcoal.

The increase in porosity with increasing addition of a crosslinking agent decreases the density of a copolymer (Fig. 20.11). Simultaneously the degree of swelling of the copolymer in toluene and similar good solvents decreases regularly (Fig. 20.12); this is an indication of an increase in crosslink density, i.e., of an increase in the concentration of crosslinks in the copolymer with increasing content of a crosslinking agent.

One would naturally ask: what is the structure of such a copolymer? Why does its porosity increase with increasing crosslink

TABLE 20.4. *Specific Surface Areas and Total Pore Volumes of Styrene/n-Divinylbenzene Copolymers, Diluent — n-Heptane*

Diluent content, %	*n*-Divinyl-benzene content, %	Specific surface area, m^2/g		Total pore volume, cm^3/g
		methanol	nitrogen	
0	4	5.1	0	0.030
0	20	17.2	0	0.072
0	60	28.6	—	0.160
0	100	62.7	0	0.080
70	4	3.2	0	0.034
70	20	55.0	70.7	0.320
70	40	85.6	—	0.480
70	60	88.4	278.4	0.460
70	100	94.2	423.8	0.440

concentration? This is unquestionably related to the method of synthesis of the copolymers, which is accomplished in solution. In this connection one would naturally ask about the influence of the nature of a solvent, and of its thermodynamic affinity for polymer.

Experiment shows that with equal solvent-to-monomer ratio in the reaction mixture and an equal amount of the crosslinking agent the porosity of copolymers increases as the quality of the solvent grows worse (p. 381). This is due to the effect of the nature of solvent on the conformations of the polymer chains and on structurization during polymerization.

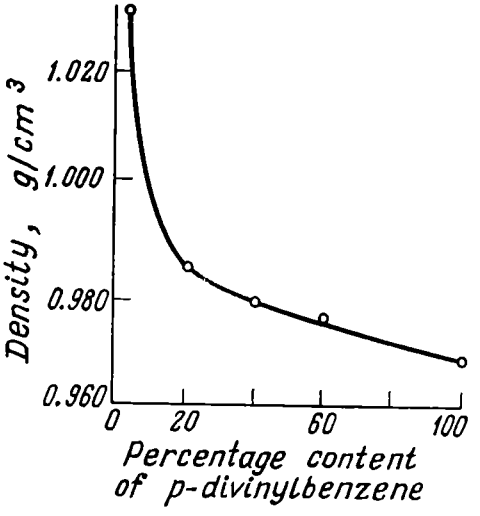


Fig. 20.11. Dependence of density of styrene/*n*-divinylbenzene copolymers synthesized in the presence of 70 per cent *n*-heptane, on divinylbenzene content

The three-dimensional polymerization occurring in the solvent results in a gel, i.e., in a binary system consisting of a spatial lattice with the solvent enclosed in it (p. 358). In such a case, as experiment shows, the system does not undergo macroseparation. Hence, the gel contains the whole amount of the solvent added, and when the latter is evaporated the volume it occupies is freed. If the three-dimensional network of the copolymer formed is ex-

tremely rigid and is preserved upon evaporation, the pore volume should be equal to the volume of the solvent that was present. Actually, however, the rigidity of the spatial lattice depends on the solvent in which synthesis occurs.

If the thermodynamic affinity of the solvent for a polymer is high, i.e., if the solvent is a good one, it plasticizes the system and the gel becomes elastic. Gels produced in poor solvents are not

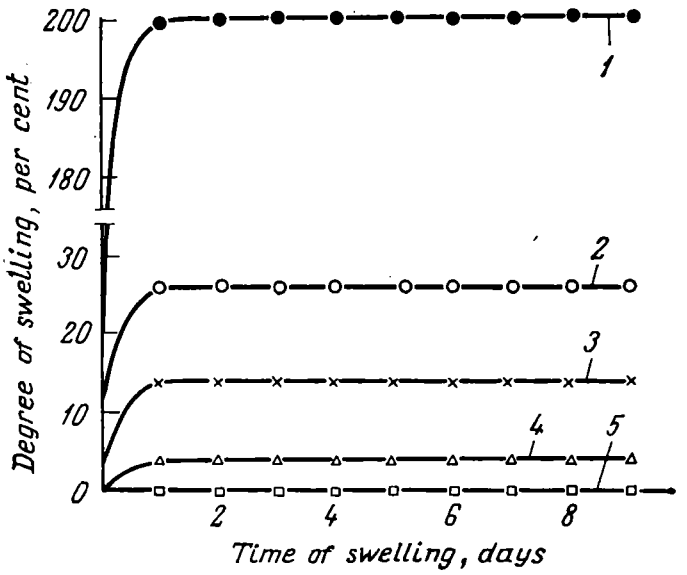


Fig. 20.12. Swelling of styrene/*n*-divinylbenzene copolymers (70 per cent *n*-heptane) in benzene:
1—4 per cent DVB; *2*—20 per cent DVB; *3*—40 per cent DVB; *4*—60 per cent DVB; *5*—100 per cent DVB

elastic but rigid. This affects the amount of shrinkage that occurs when the solvent is evaporated. Elastic gels should give higher shrinkages than nonelastic ones.

Experiments carried out by the author showed that the shrinkage of a sample containing 20 per cent DVB and 93.5 volume per cent of toluene is 44 per cent, whereas for samples produced under similar conditions in the presence of *n*-decane it is only 9 per cent. This means that when the solvent is removed from an elastic gel, the volume of the remaining voids is much smaller than in the case of a nonelastic gel.

This qualitative examination can be supported by calculations based on the idea that porosity is due entirely to the solvent removal. Then the pore volume (V_{por}) should be equal to the volume of solvent V_{solv} minus the change in volume ΔV of the sample due to shrinkage:

$$V_{por} = V_{solv} - \Delta V \qquad (20.13)$$

By the shrinkage α we shall understand the ratio of the change in volume of the gel to its total volume, equal to the sum of volumes of polymer V_{pol} and solvent V_{solv} (we assume for simplicity that the monomer is completely polymerized and that the volume of the polymer equals the volume of the monomer):

$$a = \frac{\Delta V}{V_{pol} + V_{solv}} \tag{20.14}$$

Combining Eqs. (20.13) and (20.14), we get

$$V_{por} = V_{solv} - \alpha (V_{pol} + V_{solv}) \tag{20.15}$$

Hence, the total pore volume per unit mass of the polymer

$$W_0 = \frac{V_{por}}{V_{pol} d} = \frac{\frac{V_{solv}}{V_{pol}} - \alpha \left(1 + \frac{V_{solv}}{V_{pol}}\right)}{d} \tag{20.16}$$

where d is the density of the copolymer.

Equation (20.16) shows that the total pore volume of a copolymer should be dependent on the amount of the solvent taken and on the shrinkage, which in its turn is dependent on the thermodynamic affinity of a solvent for a copolymer (its "quality") and on the degree of crosslinking of the latter.

Thus, if we substitute into Eq. (20.16) the shrinkage values found, 0.44 and 0.09, then with $V_{solv}/V_{pol} = 0.93$ for samples synthesized in the presence of toluene and *n*-decane the total pore volumes are 0.07 and 0.81 cm^3/g, respectively, which is in accord with experimental data. Hence, it follows from Eq. (20.16) that with equal polymer-to-solvent ratios the worse the solvent, the higher will always be the porosity.

On the basis of the same equation it can be shown that even in the presence of a good solvent highly developed porosity can be produced by taking considerably larger quantities of a solvent. To demonstrate this we write Eq. (20.15) for two solvents in the presence of which gels of different shrinkage α' and α'' form:

$$V_{por} = V'_{solv} - \alpha' (V_{pol} + V'_{solv})$$
$$V_{por} = V''_{solv} - \alpha'' (V_{pol} + V''_{solv})$$

If the porosity of the samples is the same, then

$$V'_{solv} - \alpha' (V_{pol} + V'_{solv}) = V''_{solv} - \alpha'' (V_{pol} + V''_{solv}) \tag{20.17}$$

Transforming Eq. (20.17), one obtains

$$V'_{solv} = \frac{V''_{solv} (1 - \alpha'') - V_{pol} (\alpha'' - \alpha')}{1 - \alpha'} \tag{20.18}$$

or

$$\frac{V'_{solv}}{V''_{solv}} = \frac{(1-\alpha'') - \frac{V_{pol}}{V''_{solv}}(\alpha'' - \alpha')}{1-\alpha'} \qquad (20.19)$$

Substituting the values $\alpha' = 0.44$ and $\alpha'' = 0.09$ into Eq. (20.19), we get the ratio of volumes of toluene and *n*-decane

$$\frac{V'_{solv}}{V''_{solv}} = 2.3$$

Thus, to ensure an equal total pore volume of about 0.820 cm^3/g with 20 per cent DVB in the mixture, about 2.3 times more of the good solvent toluene should be taken than of *n*-decane. This is in good agreement with the data of Millar, who obtained copolymers of very low density in the presence of toluene taken in the amount of 200-300 per cent of a monomer.

On the basis of Eq. (20.16) the effect of the amount of the solvent on the total pore volume at an equal degree of crosslinking, i.e., equal shrinkage, can also be shown. For this purpose we rewrite the equation as:

$$W_0 = \frac{\frac{V_{solv}}{V_{pol}}(1-\alpha) - \alpha}{d} \qquad (20.20)$$

It is clear from Eq. (20.18) that, other conditions being equal, the total pore volume of a copolymer should increase with increasing amount of solvent V_{solv} in the reaction mixture.

Macroporous resins are characterized by a definite pore volume distribution with respect to radii. The pore radii of such ion exchangers and their skeletons are of the order of 100 to 1000 Å, and in some cases may be as high as 100 000 Å.

Macroporous resins cannot replace ordinary standard resins. Both have their own fields of application. However, macroporous resins have exceptional properties. Their high porosity facilitates the diffusion of reagents through them and for this reason a large number of functional ionogenic groups can be introduced into macroporous resins to increase their exchange capacity. Macroporous resins can be used for sorbing ions from media in which they do not swell, especially from nonaqueous media. They possess increased mechanical strength and their structure does not change on drying. By means of macroporous resins large antibiotic ions and even particles of colloidal size can be removed. Thus, the problem of removing colloidal silicic acid from water can be solved by using macroporous ion exchangers.

It has been established that to remove a particle the pore must be about 65 times larger than the particle.

All that has been said above is evidence that the decisive factor in the production of the new type of ion-exchange resins are the methods of structural modification. To obtain ion exchangers of assigned properties it is necessary to know the structural features of the polymers and the nature of their interaction with solvents.

When using ion-exchange resins it is necessary to take into account their resistance to the solvents from which they are sorbing ions (ion-exchange resins should not dissolve) and their chemical resistance (ion-exchange resins should not degrade or enter into chemical reactions with the working medium). When ion-exchange resins are used at elevated temperatures, their macromolecules may undergo thermal degradation. Hence, ion exchangers should be thermally stable.

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CHAPTER 21

Gas Permeability of Polymers

Polymeric materials are often used as thickeners, protective coatings (films or varnishes), artificial leathers, membranes, and so forth. In all these cases, an important role is played by the mass transfer of gases and vapours through polymeric materials, the so-called *mass permeability*, or simply *permeability*, of polymeric materials.

There are two basic mechanisms of the penetration of gases through solids: phase and diffusion permeability.

Phase permeability is the stream of gas or vapour through some permanently existing open capillaries of a solid, e.g., through the open pore system (p. 594). In this case, gases or vapours which pass through retain their phase state. Depending on the pore size, gas stream may obey different laws. For example, if the pore diameter is considerably greater than the mean free path of gas molecules, the laminar flow of gas obeying Poiseuille's law is observed (p. 455). If the pore diameter is small in comparison with the mean free path of gas molecules, the molecular flow, or the Knudsen flow, is observed.

Diffusion permeability is an intricate process, which includes the sorption of gas or vapour by a polymer from the side of a sample which is in contact with it, the diffusion of atoms or molecules of a sorbate through the layer of a material and their separation on the opposite side. Diffusion permeability in pure form is observed when gases are transferred through nonporous and microporous membranes. In most cases, gases and vapours are transferred through a body simultaneously according to several mechanisms, and therefore the gas permeability of different materials changes within a wide range.

The values of gas permeability coefficients for several materials (at 20 °C and a layer thickness of 1 cm) are given below:

	Hydrogen permeability $cm^3 \cdot cm/(cm^2 \cdot s \cdot atm)$
Metals	10^{-17}-10^{-14}
Salts, inorganic glass	10^{-14}-10^{-10}
Polymers	10^{-10}-10^{-7}
Liquids	10^{-7}-10^{-5}
Paper, leather	10^{-5}-10
Textiles	10-10^3

It follows from these data that polymers by their gas permeability hold an intermediate place between liquids and ordinary solids. The highest gas permeability is possessed by textiles, paper, leather and ceramics, where the basic mechanism is phase permeability.

Since the processes of sorption and diffusion are important to diffusion permeability, they will be considered in detail.

21.1. GAS SORPTION BY POLYMERS

In Chap. 20, we considered in detail the processes of sorption of vapours, mainly of organic substances, by polymers. Gas differs from vapour in that it is in a state with temperature higher than the critical one T_{cr}. Permanent gases include He, H_2, N_2 and O_2. Carbon dioxide (CO_2) and ammonia (NH_3) are vapours at room temperature.

Gases, like vapours, can be adsorbed on the outer and inner surfaces of polymers, or they can dissolve in their micropores and smaller voids that originate between macromolecules (p. 606). The total amount of absorbed or sorbed gas can be measured, for example, by means of the McBain balance as described on page 595, and then the concentration c of a gas in a polymer can be calculated. It is the greater, the higher is partial pressure of gas p in the environment:

$$c = \sigma \cdot p \qquad (21.1)$$

The factor of proportionality σ is known as the sorption coefficient and is expressed by the number of cubic centimetres of gas absorbed per cubic centimetre of a polymer at a partial pressure of one atmosphere and an experiment temperature $\left([\sigma] = \left[\frac{cm^3}{cm^3 atm}\right]\right)$.

If we work with elastic or solid nonporous polymers, in respect of which only the process of gas dissolution is observed, the coefficient σ is known as the gas solubility coefficient. It depends on partial gas pressure and temperature. However, at low pressure

or elevated temperature, the values of σ can be regarded as independent of *p*. Then, Eq. (21.1) is an analogue of Henry's law.

TABLE 21.1. *Solubility Coefficients σ of Gases in Polymers at* 25 °C

Polymer	H_2	H_2	N_2	O_2	CO_2	NH_3	SO_2
Natural rubber	0.011	0.037	0.055	0.112	0.90	6.9	23.6
Butadiene-styrene copolymer (CKC-30)	—	0.031	0.048	0.94	0.92	8.1	17.2
Butadiene-acrylonitrile copolymer (CKH-27)	0.080	0.27	0.032	0.68	1.24	13.5	48.0
(CKH-39)	0.0066	0.022	0.028	0.054	1.49	—	—
Polychloroprene (isoprene)	—	0.026	0.036	0.075	0.83	8.8	18.1
Polyisobutylene	0.011	0.036	0.055	0.122	0.68	1.25	3.6
Polydimethyl-siloxane	—	0.047	0.081	0.126	0.43	—	—
Polyethylene (amorphous)	0.012	—	0.041	0.077	—	—	—

Table 21.1 gives the solubility coefficients of some permanent gases in some polymers. For elastic polymers, they are similar to the values of σ for organic liquids by the order of magnitude. This is understandable, because the mechanism of gas dissolution is the same in both of them, i.e., gas fills up the free volume, which is of a fluctuational nature, owing to which gas molecules can change places with polymer units in sorption. Gas also occupies the free volume in microporous polymers as it dissolves in them.

The partial crystallization of polymers increases the density of macromolecular packing and decreases the free volume. Voids in crystalline regions are as a rule impervious even to small gas molecules (p. 598). Therefore, gases dissolve mainly in the amorphous part of a polymer, and the solubility coefficient σ is directly proportional to its share in a polymer.

It follows from Table 21.1 that the solubility of permanent gases in polymers is small, and therefore the polymer structure does not considerably change when they are sorbed. The vapours of CO_2 and NH_3 interact with polymers more strongly, and σ is considerably greater for them. The sorption of these substances can cause noticeable changes in the structure of polymers, expressed in their swelling. For example, poly(methyl methacrylate) swells in CO_2 vapours.

The interaction of vapours of organic substances or water with polymers depends on their chemical nature. This has been considered in Chaps. 12 and 13. Nonpolar polymers better sorb the vapours of nonpolar substances and polar polymers, the vapours of polar substances and water. In this case, considerable changes occur in the structure polymers, which swell and even dissolve.

In the sorption of gases and especially vapours, the latter may condense in a polymer, i.e., they may change their phase state, becoming liquid. In some cases, the sorbate may form aggregates, or associates, in a polymer.

When gases dissolve in polymers, the polymer-polymer and gas-gas contacts are replaced by polymer-gas contacts. This process is similar to that of polymer dissolution in a low-molecular liquid (Chaps. 12 and 13). In this case, the internal energy and enthalpy of a system change, i.e., gas sorption is accompanied with the thermal effect ($Q_p = \Delta H$).

The partial enthalpy (heat) of dilution of gas $\Delta\bar{H}_1$ is equal to the difference between its partial enthalpy in a polymer $\bar{H}_1$ and the molar enthalpy of gas H_1^0. Generally, it consists of the heat of gas condensation ΔH_c and the partial heat of mixing of condensed gas with a polymer ΔH_1^M.

$$\Delta\bar{H}_1 = \Delta H_c + \Delta H_1^M \tag{21.2}$$

The heat of condensation is always negative, while the heat of mixing may have different signs, depending on the nature of a gas and that of a polymer.

According to the general laws of thermodynamics, the sign of the partial heat of dilution determines the sign of the temperature coefficient of solubility of a component.

Indeed, in the general case,

$$\frac{d\sigma}{dT} = \frac{\Delta\bar{H}_1}{T\left(\frac{\partial\mu_1}{\partial x_1}\right)_p} \tag{21.3}$$

where T = absolute temperature
$(\partial\mu_1/\partial x_1)_p$ = change in the chemical potential of a component with its molar fraction.

Both quantities are essentially positive (p. 382). Partial heats of dilution for permanent gases and vapours have different signs. For example, for permanent gases (He, H_2, N_2) that are at the temperature considerably higher than their T_{cr}, ΔH_c is small by its magnitude and the value of $\Delta\bar{H}_1$ is mainly determined by the term ΔH_1^M, which is as a rule positive. Consequently, $\Delta\bar{H}_1 > 0$. Therefore, the solubility of these gases in a polymer increases with temperature $\left(\frac{d\sigma}{dT} > 0\right)$.

The heat of condensation of gases, which are in a state with temperature lower than their T_{cr} (vapours), is comparatively great, and the total value of $\Delta\bar{H}_1$ is negative. Therefore, the solubility of CO_2, NH_3 and SO_3 in a polymer decreases with an elevation of temperature $\left(\frac{d\sigma}{dt} < 0\right)$.

21.2. GAS DIFFUSION IN POLYMERS

Diffusion is the redistribution of a substance between various parts of a system, caused by the thermal motion of molecules and atoms. There is self-diffusion and mutual diffusion.

Self-diffusion is a disorderly movement of similar molecules of a substance under the action of thermal motion. *Mutual diffusion*, or simply *diffusion*, is a mutual movement of different types of molecules, also caused by their thermal motion, but this process is ordered, directed It is observed in the presence of the concentration gradient c or, in general, the chemical potential gradient μ_i. The molecules of a given substance move from the place where their concentration c or chemical potential μ_i is greater to the place with smaller values of c and μ_i. Hence, the derivative of the concentration with aspect to distance, or the concentration gradient, is negative $\left(\frac{dc}{dx} < 0\right)$.

We have already dealt with the diffusion process when we considered the diffusion of macromolecules in a low-molecular liquid (p. 326). We will consider now the directed motion of gas or vapour in a polymer. In this case, the moving gases or vapours can, to a certain extent, interact with polymer molecules; as we have seen, there are no absolutely inert bodies (p. 600).

The mechanism of diffusion of gases and liquids is similar to that of their flow (p. 458) and consists in the periodically repeated hops of the diffusing molecules from one equilibrium position to another; this is possible if a free volume is available (p. 609). For an elementary act of a hop of the diffusing molecule to occur there must be a "hole" of the required size next to it and sufficient energy for destroying the bonds between polymer molecules, i.e., the *activation energy of a diffusion process.* Therefore, the matter in question is the *activated diffusion of gases in polymers.*

The diffusion rate is quantitatively characterized by the diffusion coefficient D, which is a proportionality factor in Fick's first law:

$$Q = -D\frac{dc}{dx}St \qquad (21.4)$$

where Q = amount of a substance that has diffused in time t through the cross-sectional area S

dc/dx = constant gradient of gas concentration in a film layer
D = diffusion coefficient which is numerically equal to Q at $S = 1$ cm^2, $t = 1$ s and $dc/dx = 1$.

However, Fick's first law cannot be used to calculate the diffusion coefficient, because the law is valid only for *stationary flow*, i.e., flow which moves at a constant rate and at a constant concentration gradient. Indeed, even if diffusion is not complicated by a strong interaction between a gas and a polymer, stationary

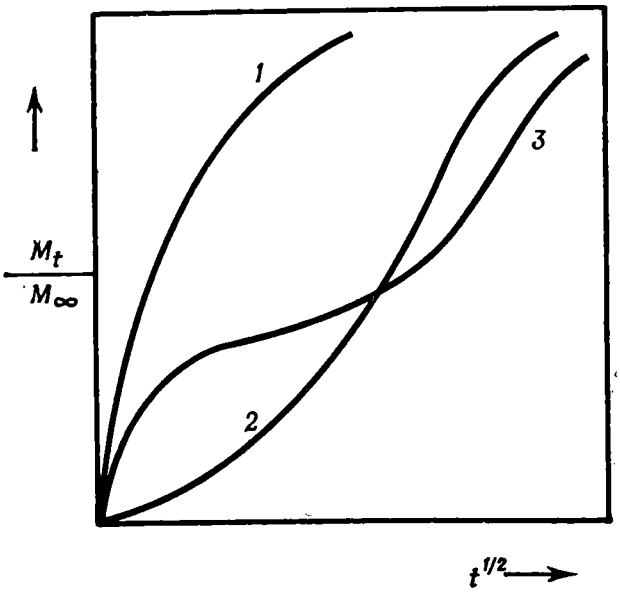

Fig. 21.1. Dependence of M_t/M_∞ on $t^{1/2}$

flow sets up in a certain time. In general, we deal with *non-stationary flow*, whose concentration gradient is not constant. In this case, Fick's second law is valid:

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{21.5}$$

which has several solutions *, depending on the boundary conditions and, consequently experiment conditions.

The most commonly used methods of determining D are the sorption-desorption method and the Dienes-Barrer method.

The sorption-desorption method consists in the study of the kinetics of gas or vapour sorption by a polymer sample under isobaric-isothermal conditions. This can always be done when the sorption coefficient is being determined (p. 630).

If the gas-sorbing sample has the form of a plate (film) with a thickness l, then, under the boundary conditions $0 < x < l$ and

* One of the solutions of this law was considered on page 503.

$0 < c < c_{equiv}$, Eq. (21.5) is solved as follows:

$$\frac{M_t}{M_\infty} = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{21.6}$$

where M_t = amount of the sorbate or desorbate by the moment of time t

M_∞ = equilibrium amount of the sorbate.

To calculate D, the graphic dependence $\frac{M_t}{M_\infty} = f(t^{1/2})$ is plotted; this dependence is usually in the form of an L-shaped curve with its initial rectilinear part in the region $\frac{M_t}{M_\infty} < 0.6$ (Fig. 21.1). The value of D is calculated by the slope of this segment.

The *Dienes-Barrer method* consists in the creation of pressure p_1 of the test gas on one side, and a vacuum, on the other, in a closed cell consisting of two metallic chambers divided by a test membrane of a polymeric material.

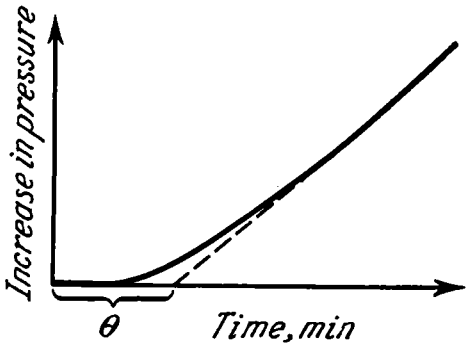

Fig. 21.2. Time dependence of the pressure of a gas diffused into a cell through a film

Gas comes into contact with one side of the membrane, and then it appears on the other side after a certain lapse of time t. Then, pressure grows and the curve $p = f(t)$ becomes a straight line (Fig. 21.2). Continuing this straight line until it intersects the abscissa axis, we obtain the segment θ, which is known as "retardation time". To calculate the diffusion coefficient, Eq. (21.5) is used, and it is integrated at definite boundary conditions from $x = 0$ to $x = l$. Then,

$$D = \frac{l^2}{6\theta} \tag{21.7}$$

The systems which obey Fick's second law, or the Fickian systems, are characterized by L-shaped plots of $\frac{M_t}{M_\infty}$ versus $f(t^{1/2})$ (Fig. 21.1). This is observed when D is a function of only the concentration, and does not depend on time.

In many cases, anomalous non-Fickian diffusion is observed; it is expressed in a different nature of the dependence $\frac{M_t}{M_\infty} = f(t^{1/2})$, which has the form of S-shaped curves or two-step curves (Fig. 21.1).

A deviation from Fick's second law is usually connected with a change in macromolecular conformation and with the displacement of structural elements of a polymer that are the result of

the interaction between its macromolecules and the molecules of the diffusing gas. Both of these processes are of a relaxational nature. If relaxation time is not great, as is the case with polymers in the elastic state, conformational and structural changes occur quite rapidly. In this case, D depends only on the rate of movement of gas molecules. At $T < T_g$, segment mobility is small and the rate of conformational and structural changes may turn out to be less than that of gas diffusion. The total effect of transfer is determined by the rate of the first processes, and D is a function of time.

As temperature rises, the kinetic energy of gas molecules, the free volume in a polymer and the thermal motion of units and chain segments increase. Therefore, the gas diffusion rate grows, i.e., the diffusion coefficient changes with temperature.

The temperature dependence of D is expressed by the exponential Frenkel-Eiring equation

$$D = D_0 e^{-\frac{\Delta G_{dif}^{\neq}}{RT}} \tag{21.8}$$

where $\Delta G_{dif}^{\neq}$ is the free energy of activation of diffusion, which is connected with the heat and entropy of activation of the process with the well-known relation

$$\Delta G_{dif}^{\neq} = \Delta H_{dif}^{\neq} - T\,\Delta S_{dif}^{\neq}$$

Therefore, Eq. (21.8) may be rewritten as follows:

$$D = D_0 e^{\frac{\Delta S_{dif}^{\neq}}{R}} \cdot e^{-\frac{\Delta H_{dif}^{\neq}}{RT}} \tag{21.9}$$

It has been shown theoretically that

$$D_0 = \frac{d^2 kT}{h} \tag{21.10}$$

where d = length of the hop
k = Boltzmann constant
h = Plank constant
T = absolute temperature.

After taking the logarithm of Eq. (21.9), we obtain

$$\ln D = \left(\ln \frac{d^2 k}{h} + \ln T + \frac{\Delta S_{dif}^{\neq}}{R}\right) - \frac{\Delta H_{dif}^{\neq}}{R} \cdot \frac{1}{T} \tag{21.11}$$

The value of $\ln T$ is comparatively small. Therefore, the temperature dependence of $\ln D$ is determined mainly by the second term. If the dependence of $\ln D$ on $\frac{1}{T}$ is rectilinear, the slope of the straight line can be used to calculate the heat of activation of

the diffusion process, while the segment that it cuts off on the ordinate axis, to calculate the value of $\Delta S_{dif}^{\neq}$.

The dependence $\ln D = f\left(\frac{1}{T}\right)$ is curvilinear in a wide temperature range, and this is connected with a change in the polymer structure with temperature. In this case, the quantity $\Delta H_{dif}^{\neq}$ is determined as a derivative in every point of the curve, and this quantity itself is a function of temperature.

21.3. DIFFUSION PERMEABILITY AND NATURE OF POLYMERS

In accordance with Eq. (21.1),

$$\frac{dc}{dx} = \sigma \frac{dp}{dx} \tag{21.12}$$

Substituting the value of dc/dx from Eq. (21.12) in Eq. (21.4), we obtain

$$Q = -D\sigma \frac{dp}{dx} St \tag{21.13}$$

At $S = 1$ cm^2, $t = 1$ s and $dp/dx = 1$, the product $D\sigma$ is usually known as the permeability coefficient, or the diffusion permeability coefficient:

$$P = D\sigma \tag{21.14}$$

The dimension $[\sigma] = \frac{cm^3}{cm^3 atm}$, the dimension $[D] = \frac{cm^2}{s}$. Consequently, the dimension $[P] = \frac{cm^3 \cdot cm}{cm^2 \cdot s \cdot atm}$ *.

According to Eq. (21.14), the permeability coefficient P can be calculated when σ and D are known. But P can be measured also directly, for example, by means of the said Dienes-Barrer method, which is used for determining D (p. 634). To this end, the slope of the rectilinear part of the curve $P = f(t)$ (Fig. 21.2) is taken to calculate the change in pressure per unit time dp/dt and, knowing the chamber volume V, the pressure created on one side of the membrane (p_1), the experiment temperature T, the area S

* In SI units, the sorption coefficient is expressed in m^2/N, D in $\frac{m^2}{s}$ and P in $\frac{m^2}{s}\left(\frac{N}{m^2}\right)^{-1}$. A transition from one system to another can be made by means of the following relations:

$$1\frac{m^2}{s} = 10^4 \frac{cm^2}{s}; \quad 1\frac{m^4}{s \cdot N} = 10^9 \frac{cm^3 \cdot cm}{cm^2 \cdot s \cdot atm}$$

and the thickness l of the membrane, P is calculated by the equation:

$$P = \frac{\Delta pV \times 273}{\Delta t\, Sp_1\, (273 + T)} \qquad (21.15)$$

Polymer permeability depends on the nature of a gas and that of a polymer, the nature of a gas affecting mainly the value of the sorption coefficient, while that of a polymer, the value of the diffusion coefficient.

The gas permeability of polymers, like their other properties, is determined by the following factors:

1. Chain flexibility.
2. Intermolecular interaction.
3. Phase and aggregation state of a polymer.
4. Density of macromolecular packing.
5. Extent of crosslinking.

Permeability is a complex function of these factors; this follows from Table 21.2, which gives the values of hydrogen permeability and the coefficient of diffusion and sorption of hydrogen for a number of polymers. This number is retained also for other diffusing permanent gases, and even CO_2.

TABLE 21.2. *Permeability and Coefficients of Diffusion and Sorption at* 20° C

Polymer	$P \times 10^1$	$D \times 10^6$	$\sigma \times 10^2$
Polydimethylsiloxane	390	—	—
Polyisoprene (smoked sheets)	34.6	7.23	4.16
Polybutadiene	27.0	8.60	3.96
Butadiene-styrene copolymer	25.2	8.80	2.69
Butadiene-acrylonitrile copolymer	9.1	4.05	2.20
Polychloroprene	8.1	3.18	2.25
Polystyrene	6.9	4.62	2.44
Polyisobutylene	4.0-4.5	2.42	2.07
Polyethylene	5.9	2.08	1.88
Polypropylene	4.2	—	—
Polyvinyl chloride	2.3	2.71	0.54
Polyvinylidene chloride	0.06	—	—
Polyvinyl alcohol	0.01-0.04	—	—
Cellulose hydrate	0.008-0.01	—	—
Cellulose acetate	2.50	—	—
Cellulose nitrate	2.30	—	—

Table 21.2 clearly shows that polymer chain flexibility and interchain interaction are determinative in diffusion permeability.

High equilibrium and kinetic flexibility of a polymer chain and the presence of only dispersion interaction are conducive to high values of D and P. This is natural, because the thermal motion of chain units (segmental motion) facilitates the movement of gas molecules. Owing to the comparatively weak interchain interaction, the activation energy of diffusion is not large, and therefore high values of D and P are observed. Hence, it is understandable that the greatest gas permeability is possessed by polymers in a rubber-like state (Chap. 7), especially by polymers which have a double bond in their chain.

If polymers have the main chain, the introduction of such substituents as —Cl, $-C_6H_5$, —OH, $-C{\equiv}N$ does not cause a change in the equilibrium flexibility of the chain (p. 103). But the nature of a substituent can greatly change interchain interaction, whose intensification always causes a decrease in the free activation energy of diffusion and in gas permeability. This is evident from the example of nitrile rubbers: gas permeability decreases with an increase in the percentage of the polar groups $-C{\equiv}N$. A similar effect is caused by the introduction of comparatively small quantities of chlorine atoms: the gas permeability of polychloroprene is smaller than that of polybutadiene and *cis*-polyisoprene. Consequently, an increase in interchain interaction causes a decrease in gas permeability even within the limits of a rubber-like state.

In this respect, elastomeric polyurethane is of certain interest. Notwithstanding the high flexibility of its chain and well-pronounced rubber-like properties, its nitrogen permeability is about 20 times less than that of natural rubber owing to the formation of strong interchain hydrogen bonds.

As temperature drops, the polymer passes over from an elastic to a glassy state (Chap. 8), which is characterized by considerably less mobility of its units. Owing to this and to stronger interchain interaction, gas permeability of the same polymer at $T < T_g$ is less than that at $T > T_g$.

However, polymers which are in a glassy state at room temperature and which even have approximately the same T_g, e.g., polystyrene (PS) and poly(vinyl chloride) (PVC), have different permeability. Apparently, this is due to the difference in macromolecular packing density, which is less for PS than for PVC (p. 168).

Macromolecular packing density affects gas permeability, whose value is the greater, the looser is molecular packing. Therefore, any factors which hinder dense packing, e.g., chain branching, are conducive to high values of gas permeability.

If flexible macromolecules can form dense packing, gas permeability decreases. Apparently, this explains the low gas permeability of polyisobutylene.

The greatest packing density is possessed by crystalline polymers (p. 168). Therefore, such crystalline nonpolar polymers as polyethylene or polypropylene have smaller values of gas permeability than polyisoprene or polybutadiene.

Especially low values of permeability are observed for crystalline polymers with strong interchain interaction, such as poly(vinylidene chloride) and poly(vinyl alcohol), between whose chains the hydrogen bonds are formed. Strong interchain interaction and chain rigidity of cellulose hydrate are conducive to very low gas permeability, although the macromolecules of this polymer are not very densely packed.

A special place among all polymers is held by poly(dimethyl siloxane), for which the coefficients of permeability and diffusion of all gases are higher by several orders than those of natural rubber (Table 21.3). This is due to: (a) high chain flexibility, which is consequence of a small potential barrier of rotation around the bond —Si—O— (Chap. 4); (b) weak intermolecular interaction, and (c) loose packing of atoms in a chain, as indicated by the low relative density of polyorganosiloxanes, notwithstanding the presence of heavy silicon atoms in their molecules.

TABLE 21.3. *Values of P, D and σ Coefficients for Gas-Polymer Systems at* 20 °C

Polymer	N_2			H_2			O_2			CO_2		
	$P \times 10^8$	$D \times 10^6$	$\sigma \times 10^2$	$P \times 10^8$	$D \times 10^6$	$\sigma \times 10^2$	$P \times 10^8$	$D \times 10^6$	$\sigma \times 10^2$	$P \times 10^8$	$D \times 10^6$	$\sigma \times 10^2$
Dimethyl-siloxane	188	23.3	8.1	390	83	4.7	380	30	12.6	1.635	38	43
Natural rubber	5	0.9	5.5	32	8.4	3.8	14	1.4	10.2	82	0.8	105

The gas permeability of polymers decreases as the number of crosslinks or the extent of crosslinking increases.

The foregoing applies to the permeability of gases and vapours, which comparatively weakly interact with polymers, i.e., gases and vapours whose sorption coefficient is comparatively small.

When vapours strongly interact with polymers, their permeability is mainly determined by the value of the sorption coefficient, and permeability is the greater, the higher is σ. For example, cellulose swells in water vapour, and therefore its water permeability is considerably greater than that of natural rubber, which does not swell in water vapour. Water permeability of the least hydro-

philic materials is $\sim 10^{-7}$, while that of the most hydrophilic ones (cellulose, etc.), 10^{-2} $cm^3 \cdot cm$, i.e., it differs by six orders. As liquid polarity increases, P of rubbers decreases, while that of cellulose grows.

21.4. EFFECT OF SOME FACTORS ON POLYMER PERMEABILITY

Temperature Effect. Since the heat of dilution ΔH of fixed gases is not great in a polymer, the solubility coefficient does not change sharply with temperature (Eq. 21.3). The diffusion coefficient changes with temperature considerably greater, and this causes a change in the permeability coefficient, which is connected with temperature by the equation

$$P = P_0 e^{-\frac{\Delta G^{\neq}_{per}}{RT}} \tag{21.16}$$

where $\Delta G^{\neq}_{per}$ = free activation energy of permeability.

According to Eq. (21.16), gas permeability decreases with an elevation of temperature.

Effect of Low-Molecular Liquids and Plasticizers. Gas permeability is strongly affected by liquids, especially plasticizers, present in a polymer.

The pre-absorption of low-molecular liquids by a polymer always increases gas permeability. This is because (1) liquids which are readily absorbed by a polymer as a rule plasticize it, i.e., they promote the realization of chain flexibility, and (2) the free volume of low-molecular liquids is greater than that of a polymer (p. 172), owing to which gas diffuses through the liquid. This effect is observed when moisture is absorbed by many hydrophilic polymers, e.g., cellulose and poly(vinyl alcohol), whose gas permeability in the moistened state is considerably greater than in the dry state. When some hydrophilic polymers considerably swell in water, they become gels (p. 359), and gases diffuse also through the liquid. In some works, an increase was observed in the rate of diffusion of vapours of organic substances into moistened polymers, e.g., acetone vapours.

Gas permeability of nonpolar polymers, which absorb an inconsiderable amount of water, practically does not change when they are in the dry and moistened states. But their gas permeability grows when they preliminarily sorb the vapours of CCl_4 or hexane, i.e., liquids which plasticize them. For example, in the presence of these substances, nitrogen and oxygen permeability of polyethylene grows.

For the same reason, gas permeability of plasticized polymers is greater than that of nonplasticized ones. This was observed on cellulose acetate film plasticized by alkylphthalates, on plasticized

polychlorotrifluoroethylene, and others. Plasticized polymers, particularly plasticized PVC and cellulose ethers, possess high moisture permeability. In this case, when the molar content of a plasticizer is the same, gas permeability is the greater, the larger is the alkyl radical.

Effect of Fillers. The effect of fillers on gas permeability of filled compositions is very complex. For example, the gas permeability coefficient decreases considerably when powdery fillers are introduced into polymers in quantities of up to 5-10 per cent. The value of P continues to diminish, but considerably less rapidly, when the content of a filler is increased further to 20-30 per cent by volume. Permeability grows sharply when the content of a filler is high (40-50 per cent). Such an extremum nature of permeability is connected with the complexity of the mechanism of gas transfer in a heterogeneous system, i.e., the polymer-filler system. In heterogeneous systems, the basic phase which determines gas transfer through a material is the continuous phase of a system, in this case the polymer phase. Usually, polymer molecules are adsorbed on the filler surface, and then more densely packed structures are formed that possess less gas permeability. When the content of a filler in the polymer phase is high, apparently ruptures appear, i.e., its continuity is interrupted. In a highly filled polymer, open capillaries are formed that ensure phase gas transfer: diffusion permeability is replaced by the molecular or viscous flow of gas

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